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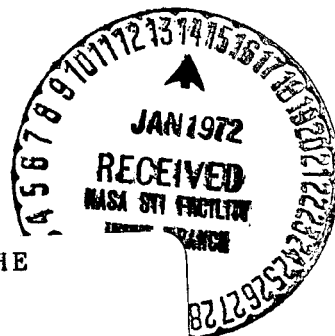
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LOSS OF ACTIVITY OF THE OXYGEN ELECTRODE BASED ON
THE SILVER CATALYST/PTFE SYSTEM

M. Cenek, O. Kouril

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ABSTRACT: Effects of electrolyte impurities and impurities from dissolution of cell components on the activity of the oxygen electrode in strongly alkaline electrolytes were determined because of the decrease in performance of low-temperature fuel cells with time. Determination was a prerequisite for using oxygen electrodes prepared from silver catalyst polymeric binder blends. Results showed, however, that the oxygen electrode of this composition is practically useless for application in electrochemical systems.

1. Introduction

As stated by Austin [1] the main disadvantage of the low-temperature fuel cells is the short life of their electrodes arising from the loss of catalyst activity. The useful life of the electrodes is an important factor in the evaluation of all types of fuel cells. According to Austin [1], the common causes of the decrease in performance with time are the following: /3*

- (a) Activity loss of the catalyst due to electrolyte impurities.
- (b) Activity loss of the catalyst due to impurities arising from the dissolution of the cell components
- (c) Disintegration of the electrodes due to slow corrosion
- (d) Loss of contact between the catalyst and the current collector
- (e) Recrystallization of the catalyst resulting in the loss of active electrode surface
- (f) Loss of wettability

For these reasons, it was necessary to determine the respective effects of the electrolyte impurities, as well as of the impurities arising from the dissolution of cell components, on the activity of the oxygen electrode in a strongly alkaline electrolyte as a prerequisite for using oxygen electrodes prepared from silver catalyst/polymeric binder (eg. PTFE) blends.

2. Theoretical Part

Concentrated aqueous solutions of alkali hydroxides are frequently employed as electrolytes in electrochemical sources. The division of metals into amphoteric and non-amphoteric, depending on the behavior of the corresponding hydroxides in alkaline media, is not quite precise for highly concentrated, i.e., 6-10 N, solutions. The behavior of the hydroxides of nonamphoteric metals in concentrated electrolytes resembles more closely the chemical

*Numbers in the margin indicate pagination in the foreign text.

properties of these metals in nonaqueous media, e.g., in melts. The hydroxides of the common non-amphoteric metals are partially soluble with the formation of the corresponding anions. Under the above conditions it is possible to speak of a "partial amphoteric character" of these metal hydroxides. The concentration of dissolved metal ions is relatively low, being of the order of 10^{-4} N. The question remains, however, if even such a low concentration may influence the activity of the catalyst.

2.1 Properties of Non-amphoteric Metals in Concentrated Solutions of Alkali Hydroxides.

Very few articles have been published concerning the behavior of non-amphoteric metals in alkali hydroxide solutions in the presence of oxygen.

The behavior of Pt cathodes in strongly acidic medium in the presence of oxygen was studied by Austin [1]. This author reported that oxide layers start to form on Pt cathodes on contact with oxygen at potential values in excess of 0.8 V (vs. NHE). The oxide film formed over a long period may acquire sufficient thickness to reduce the oxygen ionization to such an extent that, due to side reactions, a zero-load electrode potential of 1.0 to 1.1 V results instead of the standard O_2 potential of 1.23 V.

In contrast to these findings, gold does not form this undesirable oxide layer up to potential values of approx. 1.45 V, but the ionization rate of oxygen on gold is much lower than that on Pt.

The findings concerning the electrochemical reduction of oxygen on Pt have been summarized by Bockris [2]. Since Pt attains a potential of 0.9 V in acid media while the standard potential of the oxygen electrode is 1.23 V, this electrode will be thermodynamically unstable and may undergo dissolution. The standard potentials of all solid metals have values below 1.23 V. Therefore, no metallic support meets the insolubility requirement. In addition to the four-electron oxygen reduction process, oxygen also undergoes the reduction to hydrogen peroxide, and, eventually, hydrogen peroxide is reduced to water. These are the most important reactions occurring during the reduction of oxygen. There exists, however, an entire series of other reactions involving oxygen and the atoms of the metallic component leading to the formation of a large number of intermediate products as parts of the overall reaction, espe-

cially at high overpotentials. These products are the cause of the formation of "impurities" in the solution phase. Reactions with the potentials exceeding 0.98 V belong into the category of the four-electron reduction of oxygen, or the category of the oxidation of impurities. The reactions of oxygen reduction are highly sensitive to all impurities which may either be present immediately from the start, or may accumulate as a result of the functioning of the electrode. For this reason, the reversible potential of the oxygen reaction on the electrode was not observed until 1956. The reversible potential of 1.23 V was observed on a Pt electrode in an acid medium by Bockris and Huq. It was established that, in order to obtain the reversible potential, the concentration of the impurities in solution must be very low, since, as reported by Giles [19], impurities in amounts of 10^{-10} moles may completely cover 1 cm^2 of electrode surface.

The findings of Austin [1] and Bockris [2] on Pt are of importance with respect to the high electropositivity of platinum. If oxide films are formed on the surface of the Pt electrode at the anodic potentials of approx. 1 V, it may be expected that such oxide films will also be formed on the less noble metals, e.g., silver. The metallic support of the oxygen electrode may either dissolve by itself, or through the intermediacy of the surface oxide films which is much easier, since the solubilities of the oxides are higher.

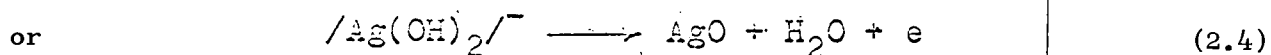
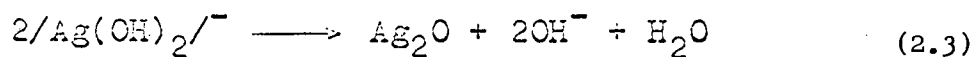
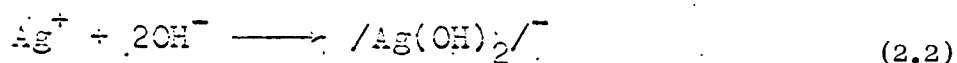
This fact must be taken into consideration especially in the case of silver. On the basis of the analysis carried out by Schwartz and Ward [3], it became apparent that it is necessary to employ either Pt or Ag in the oxygen reactions of contemporary low-temperature fuel cells. It would be possible to speak of Pt as an economically suitable material only if the ratio of metal to filler could be reduced to 1/10 of that presently used. Therefore, from the practical point of view, only Ag remains a suitable catalyst and this determines, in turn, the use of an alkaline medium as the electrolyte.

2.2 Solubility and Stability of Silver in Strongly Alkaline Solutions

In evaluating the publications in this area, it is also necessary to take into account some papers in the areas of accumulators, particularly those containing Ag/Zn. For example, Koba [4] reports that the positive electrode contains at all stages of its activity, as well as in the zero-load state, a

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mixture of Ag^{I} and Ag^{II} oxides and metallic Ag. It is apparent from the determination of the solubilities of silver oxides in 10 N KOH that maintaining Ag/Zn accumulators in the zero-load state for long periods of time results in saturation of the electrolyte with silver which is present in the form of the soluble anion $[\text{Ag}_3\text{O}(\text{OH})_2]^-$ [5]. Dirkse [6] studied the factors which determine the quantity of silver being transferred into the electrolyte in the course of the activity of the secondary alkaline silver battery by a radiometric method employing radioactive silver, as well as by a potentiometric method using komplexon I*. Dirkse showed that, in addition to the dissolution of silver oxides in the electrolyte, deposition of these oxides on the electrode from the soluble anionic form takes place at the same time. The deposition of these oxides may be expressed by the following equations:



The reactions (2.3) and (2.4) proceed with greater ease with increasing positive potential of the silver electrode.

The tendency for the formation of colloidal silver from dissolved Ag^{I} was evaluated by Rile [7].

The dissolution of non-amphoteric metals in concentrated alkaline electrolytes was demonstrated in a series of subsequent papers. Thus, for example, Young [8] mentions the heavy corrosion of the oxygen electrode prepared from porous Ni. Wagner [9] observed the "poisoning" of the air cathode by dissolved anions of the type $[\text{Cd}(\text{OH})_3]$. Klemm likewise confirms in his paper [10], the existence of dissolved anions Fe^{III} , Co^{III} , Ni^{III} , and Cu^{III} , in the respective forms $[\text{FeO}_2]^-$, $[\text{CoO}_2]^-$, $[\text{Ni}_2\text{O}_5]^{4-}$, and $[\text{CuO}_2]^{2-}$.

* Translator's Note: Komplexon I is a chelating agent of the ethylenediamine tetraacetate (EDTA) type.

The above-mentioned papers confirm that non-amphoteric metals, such as Ag, Cd, Fe, Co, Ni, Cu, etc., for example, may form (either under the influence of oxygen, or as a result of anodic oxidation) the corresponding soluble anions. These findings indicate that the amphoteric nature of the metal depends, above all, on the medium in which the metal is placed.

In the case of the amphoteric metals, a slow dissolution of the metals themselves takes place in the concentrated solutions of alkali hydroxides by the action of corrosion, e. g. in the case of Zn.

From the point of view of our objectives, i.e. the preparation of an O_2 electrode on the basis Ag catalyst/plastic, we decided to aim our work at a more detailed investigation of the behavior of Ag in strongly alkaline electrolytes.

2.2.1. Oxidation of Silver in Alkaline Solution

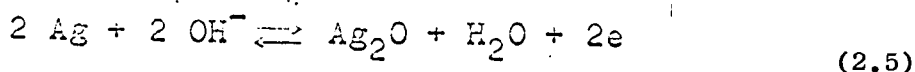
The anodic oxidation of Ag in alkaline solutions is a two-state process [11, 12, 13, and 14]. Initially, a layer of monovalent silver is formed on the metal surface in the form of Ag_2O . On attaining the critical thickness, oxidation of Ag_2O to AgO will begin. Further oxidation leads to the evolution of oxygen at the electrode. There are suppositions concerning the formation of unstable "higher oxides" during prolonged anodic oxidation, especially at high current densities [15]. In the course of the second oxidation stage, additional significant amounts of Ag_2O are formed concurrently [16].

The standard potential of the Ag/Ag_2O system in alkaline solutions is 0.342 V [17], whereas the standard potential of the Ag_2O/AgO system is 0.604 V [18]. The potentials listed are vs. NHE.

In spite of numerous studies of the anodic oxidation of silver in alkaline media, the first-stage oxidation of Ag was not thoroughly explained. This was due to the fact that all investigations were carried out with layers exceeding the thickness of several monolayers.

Giles [19] studied the oxidation kinetics of smooth silver and of pure single crystals of silver in the region of the formation of the first Ag_2O layer with the aid of impedance, potentiostatic, and electron-diffraction

measurements. It was shown that the dissolution of the silver electrode yields $[\text{Ag}(\text{OH})_2]^-$ which is preceded by the formation of Ag_2O on the electrode. The first-stage oxidation of silver to Ag_2O proceeds in two steps. Initially a monomolecular layer of Ag_2O is formed according to the equation

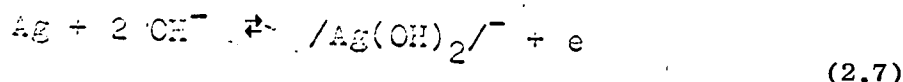


where the reversible potential of this layer is

$$E_M = -8 \pm 3 \text{ mV (vs } \text{Ag}_2\text{O/Ag)} \quad (2.6)$$

The monomolecular layer increases with time to yield a thicker layer.

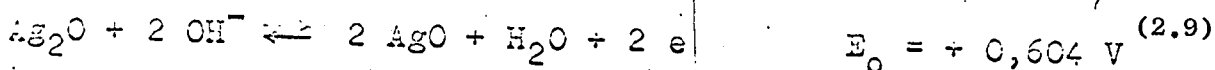
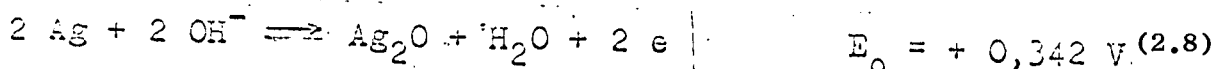
The dissolution of silver proceeds according to Giles by the dissolution reaction



and continues to a lesser extent even through the Ag_2O film. In the course of 8 the formation of the monomolecular layer of Ag_2O and during the subsequent growth of the Ag_2O film, no effect on the rate of the redox process was observed.

From the measurements of the double layer capacity and of the internal resistance of the Ag electrode during the formation of the Ag_2O film it was concluded that the double layer capacity decreases and the internal resistance increases during the formation of the Ag_2O layer. This indicates that an insulating or passivating film is formed, even though the specific conductivity of the Ag_2O film is $10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$. The internal resistance starts to decrease as soon as the formation of AgO begins. This decrease is connected with the hardening of the Ag_2O layer and the appearance of the AgO layer. The specific conductivity of AgO is $7 \cdot 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ and it increases with increasing temperature [20].

If the Ag electrode contains metallic Ag as well as AgO, the following reactions must take place at the potential of +0.262 V, according to the authors [21, 22].



The resulting reaction is given by the equation



The mechanism of formation and reduction of Ag_2O and AgO remains a controversial subject.

The published x-ray data [23] indicate that

- (a) Ag_2O forms a nucleus on the surface of Ag and grows which in a random fashion, without preferred orientation; it was not proved that charging or discharging is accompanied by the formation of a suboxide, or of a solid solution of oxygen and silver
- (b) AgO is formed as a distinct second phase without the deformation or modification of the Ag_2O lattice; similarly, Ag_2O appears during discharge as a distinct, independent phase and does not arise by way of the disintegration of the AgO lattice. /9
- (c) AgO grows at the surface of Ag_2O during the charging cycle and conversely, Ag_2O is formed at the surface during the discharging cycle
- (d) AgO is not reduced directly to Ag .

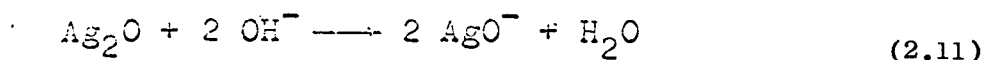
Extensive microscopic and x-ray studies of the crystallographic changes during the more than 200-fold charging/discharging cycles of the Ag electrode, carried out by Wales and Simon [24], have shown that by structural comparison with an unused sintered silver electrode, the investigated electrodes underwent only a change in the size of the Ag particles, thus adversely affecting the uniform structure of the electrode.

2.2.2. Solubility of Silver Oxides in Alkaline Solutions

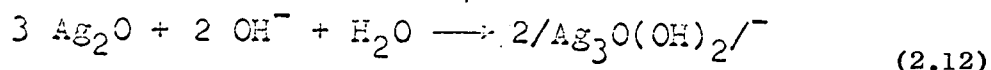
The investigation of the solubility of silver oxides in alkaline solutions was to us of extraordinary importance. It is this factor that determines, for example, the durability of the Ag/Zn battery and it is highly probable that it also strongly affects the durability of the oxygen electrode based on the Ag catalyst.

Very precise determinations of the solubility of Ag_2O in alkaline solutions were carried out by Johnston [25]. Johnston's measurements extended only

to 6 N solutions of OH^- ions. This author supposed that, in alkaline solution, soluble ions are formed from Ag_2O according to the following equation:



The existence of AgO^- ions was made doubtful by the investigation of Pleskov [26]. This author proved that Ag^{I} ions form trinuclear monovalent negative complexes in alkaline solution according to the equation



The existence of these trinuclear complexes was confirmed polarographically and potentiometrically by Koba [4]. Koba determined the solubility of Ag_2O for various concentrations of KOH at 25° with the aid of the radioactive isotope Ag^{110} . The results obtained are given in Figure 1 [4]. The solubility of Ag_2O increases with increasing temperature and the temperature dependence of the solubility of Ag_2O in 10 N KOH is given in Figure 2 [4]. /10

Amlie [13] studied the solubility of Ag_2O in the KOH concentration range from 1 to 14 mole/liter by the potentiometric method. The solubility data in KOH solutions at 25° are shown in Figure 3 [13].

Amlie's values [13] are in agreement with Johnston's [25], but these values differ from those reported by Koba [4]. More recently, these data were again reexamined by Giles [19] who determined the Faraday-impedance values and showed that at the 1M OH^- ion concentration Ag_2O dissolves in the form of $[\text{Ag}(\text{OH})_2]^-$ ions in a concentration of $1.5 \cdot 10^{-4}$ M which value is in very good agreement with the data of Amlie and Ruetchi [13].

The above authors [19] showed that the main result of the dissolution of Ag_2O is the formation of $[\text{Ag}(\text{OH})_2]^-$ ions. Other entities may appear at higher concentrations of OH^- ions. According to [19], Antikainen determined the solubility of Ag_2O in OH^- ion solutions by radiochemical methods. This investigator proved that the dissolved silver is fully converted into the $[\text{Ag}(\text{OH})_2]^-$ form, provided that the OH^- ion concentration does not fall below 0.5 M. These authors suppose that at a concentration of the OH^- ions of 0.5 M*, a small amount

* Translator's Note: Probably should be >0.5 M.

of $[\text{Ag}(\text{OH})_3]^{2-}$ ions may also be present. Other possible entities, such as Ag^+ or AgOH , for example, are formed in concentrations that are 100 times lower (of the order of $10^{-6}N$) with respect to the concentration of $[\text{Ag}(\text{OH})_2]^-$.

Amlie and Ruetschi [13] also report that all solutions containing Ag_2O exhibited a small Tyndall effect indicating the presence of colloidal Ag_2O particles. The results reported by these authors are in agreement with those reported by Johnston [25].

Amlie and Ruetschi [13] likewise measured the solubility of Ag_2O in solutions which also contained stannate ions. These authors proved that the presence of stannate in the KOH solutions had only a negligible effect on the solubility of Ag_2O . Koba and Balashova [4] also reported that the presence of zincate ion is without influence on the solubility of Ag_2O .

Cd shows very similar behavior in strongly alkaline solutions to that of Ag. Cd^{II} has a very small but finite solubility. Since the literature data concerning the solubility were not in mutual agreement, Visco and Sonner [27] decided to reinvestigate the solubility and stoichiometry of Cd^{II} in KOH with the aid of the atomic absorption and polarography of Cd^{II} . The resulting data are shown in Table I [27]. On the basis of the results obtained, the hypothesis was formulated concerning the stoichiometry of the Cd^{II} complex which exists in the form $[\text{Cd}(\text{OH})_3]^-$ in the investigated concentration range of KOH.

TABLE I. SOLUBILITY OF Cd^{II} IN KOH AS DETERMINED BY ATOMIC ABSORPTION [27].

KOH /M/	$\text{Cd}^{\text{II}}/\text{M} \times 10^{-4}/$
1.0	0.08
2.5	0.22
3.8	0.35
5.7	0.71
6.8	1.18
7.1	1.05
9.15	1.50
10.24	2.00
11.40	2.20
12.90	3.00

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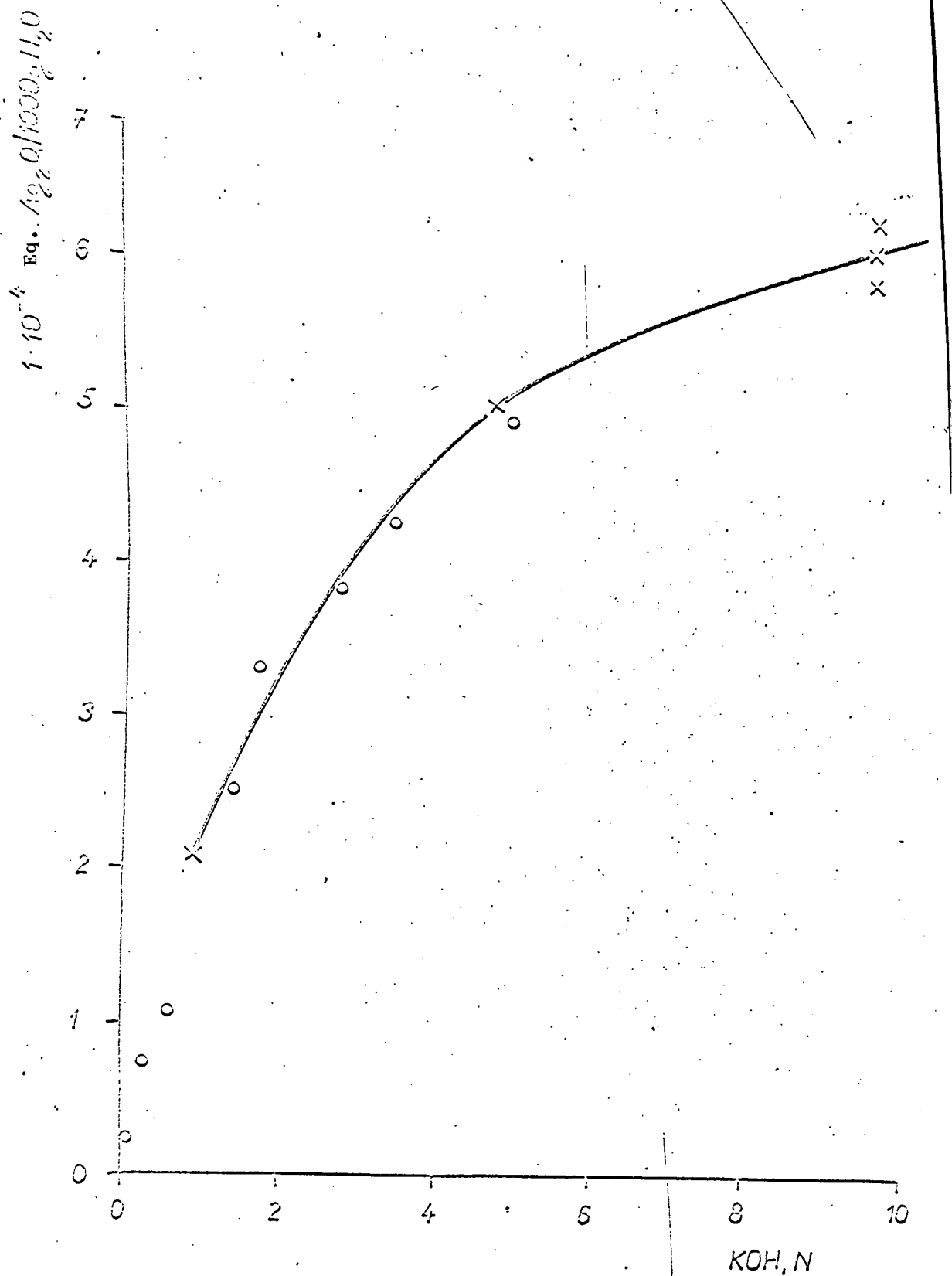


Figure 1. Dependence of the solubility of Ag_2O on the KOH concentration at 25°C [4].

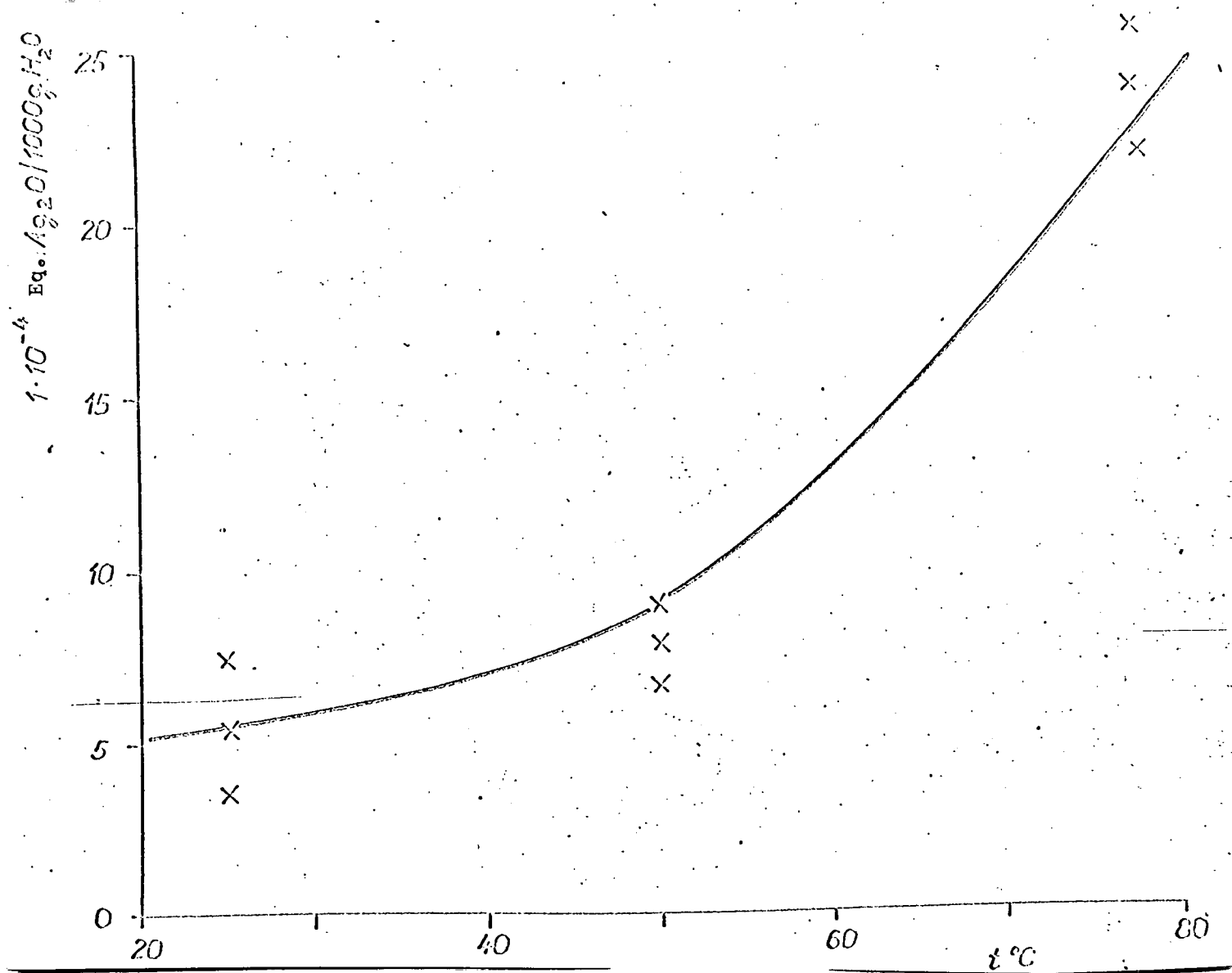


Figure 2. Dependence of the solubility of Ag_2O in 10 N KOH on temperature [4].

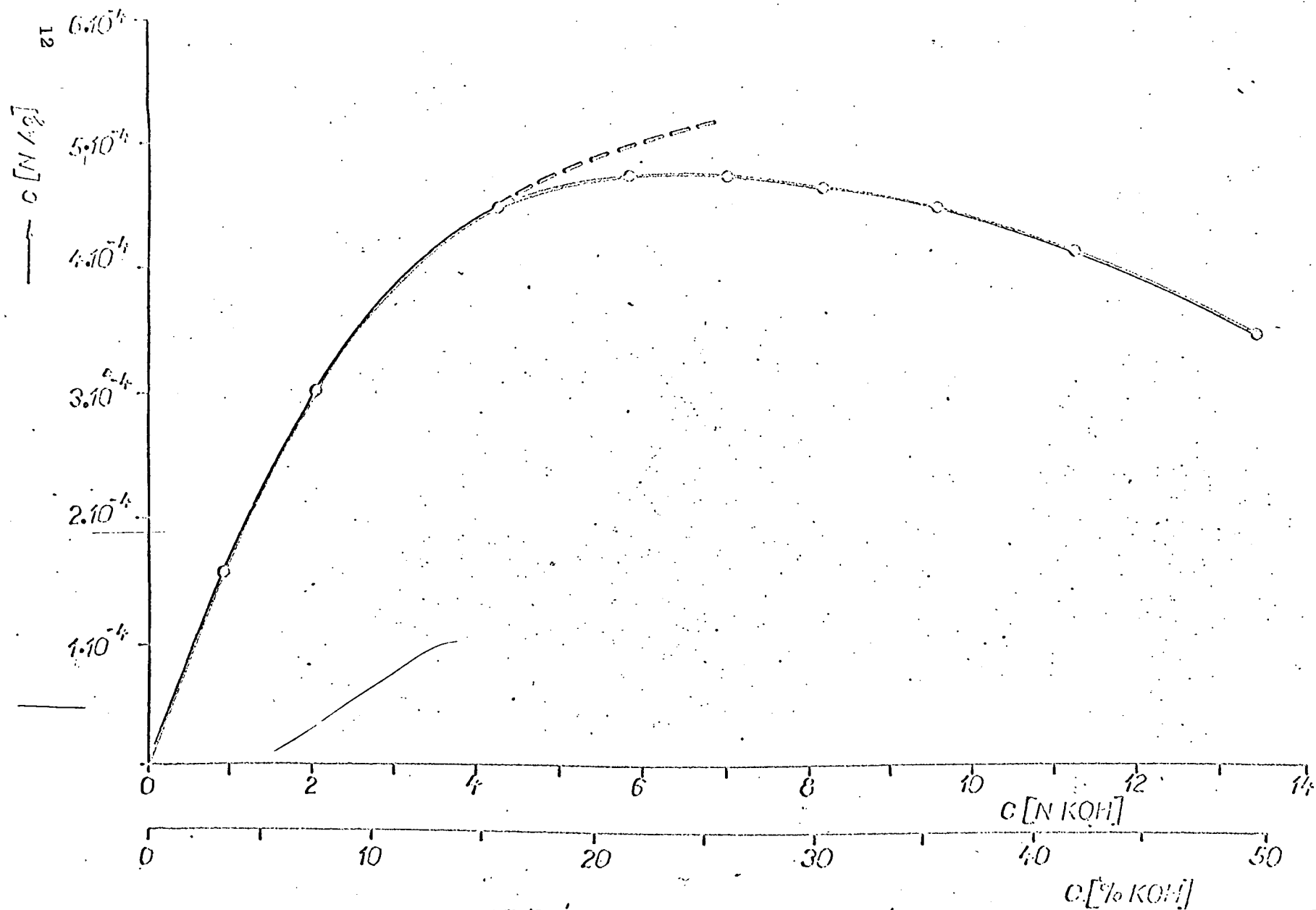


Figure 3. Solubility of Ag_2O in KOH as determined by potentiometric titration at 25°C . [13].

Solid AgO is thermodynamically unstable in alkaline solutions [11, 13]. The decomposition of AgO occurs according to the following overall reaction:



In spite of its thermodynamic instability, AgO decomposes in alkaline solutions very slowly, probably due to the O_2 overvoltage and the possibility of the formation of a protective surface coating from Ag_2O decomposition product. Pleskov and Kabanov [26] investigated the instability of Ag^{II} in alkaline solutions by using a rotating-disc electrode. These investigators found that the Ag^{II} quantity that could be present in the electrolyte was not measurable by polarographic methods. Amlie and Ruetschi [13] studied the decomposition of AgO in alkaline solutions in more detail. The decomposition was studied by a sensitive microvolumetric method. These authors studied the effects of the KOH concentration, light, presence of $[\text{Zn}(\text{OH})_4]^{2-}$, and of the method of preparation of Ag_2O . It is possible to conclude from the results obtained that the decomposition of AgO could significantly contribute to the spontaneous discharge of the Ag/Zn accumulator

Although some authors reported that the solubility of AgO in alkaline solutions is comparable with the solubility of Ag_2O [4, 9], the results of Amlie and Rutschi [13] and of Hammer and Craig [17] indicate that the solubility of AgO is negligible. If the presence of silver is detected in alkaline electrolytes which are in contact with AgO, it must be Ag^{I} resulting from the decomposition of AgO. /15

2.3 Catalyst Surface

In a study of electrode reactions it is necessary to have a knowledge of the nature of the electrode surface involved and of the changes that occur in the electrode surface due to changes of the electrode potential. This requirement becomes very important in a study of the reduction of oxygen by the action of complex compounds which are formed from the oxides produced in the potential range in which the reaction takes place. An investigation of the dependence of the reduction of oxygen on the nature of the electrode surface is a large and complicated area requiring a separate study which is not a part of the

present paper. We were mainly concerned with the changes occurring at the catalyst surface of the oxygen electrode in strongly alkaline media in the loaded and the unloaded states.

2.3.1. Surface of the Pt Catalysts

All studies of electrode reactions involving the reduction of oxygen contain significant deficiencies due to inadequate knowledge of the nature of the electrode surface where these reactions take place. The acquisition of this knowledge is not a simple matter, as indicated by the following review.

Bockris [2] investigated the changes of the Pt surface and reported that the following stages may be identified during reactions involving the reduction of oxygen:

- a) Oxygen or oxygen-containing materials, -OH , for example, are absorbed at the surface.
- b) Oxides are formed at the surface. These oxides may be two- or three-dimensional.

Adsorbed oxygen

This state of the surface involves the presence of -O (or -OH , etc.) which is bonded to the atoms of the metallic support. The adsorbed -O exists at the surface as a separate, isolated particle. It may be supposed that some of these /16 particles are relatively immobile. It is characteristic of adsorbed particles that these particles are never surrounded by metal atoms in the adsorption plane, are never in contact with one another, and are mutually free and independent.

Oxides

A characteristic of the two-dimensional oxides is that some of the metal atoms leave the original lattice of the support and form a new arrangement jointly with the oxygen atoms which is similar to that of the oxide layer. This situation may arise only in the case of the surface coverage by oxygen particles to a lesser extent than monolayer coverage. In the case of the monolayer, two adsorbed particles (e.g. -O) are present for every metal atom at the surface. A greater coverage must give rise to the growth of three-dimensional particles. Three-dimensional oxides are formed in the form of plates in some surface areas.

The information concerning the surface of the metal support is difficult to obtain because convenient methods for studies of them are unavailable. Bockris [2] gives a review of the methods for the investigation of platinum surfaces:

a) X-ray diffraction

Pt that had been polarized by a high potential (approx. 1.9 V) did not exhibit any diffraction patterns due to surface oxides. This may indicate that, the oxide platelets either are smaller than 50 Å, or possess an amorphous basic structure.

The presence of some oxides may be demonstrated by electron diffraction, but only in those cases where the oxides do not decompose in the vacuum required by electron microscopy.

b) Coulometry

This technique yields the number of coulombs required for the removal of the surface phase, but does not furnish any unambiguous information concerning the oxygen-containing particles and does not provide any direct indication about the nature of the oxide film.

The surface coverage of a pre-reduced platinum electrode, held at a constant potential in an acid medium, changes with the partial pressure of oxygen and the corresponding relationship obtained is given in Figure 4 [2]. The maximum coverage is almost achieved at a partial pressure of oxygen of about 0.3 atm. This degree of coverage corresponds to approx. $110 \mu\text{C}/\text{cm}^2$ which is considerably less than the value corresponding to the formation of a monolayer (approx. $500 \mu\text{C}/\text{cm}^2$). Every partial pressure of oxygen corresponds to a certain electrode potential value. Thus, a relationship exists between the degree of coverage and the corresponding potential attained. This relationship is pictured in Figure 5 [2]. A similar relationship is obtained under the conditions of static potential. It is evident that at the potential values below 0.75 V the Pt surface coverage is very limited. The coulometric data for the region from 1.0 to 1.7 V are shown in Figure 6 [2]. In this region also exists an almost linear relationship between the degree of surface coverage and the electrode potential. /18

In evaluating the relationship between the degree of coverage (θ) and the electrode potential (V), it was established that important differences exist in the relationships corresponding to the potential regions above 1.0 V and below 1.0 V, respectively.

According to Laitinen and Enke [2], under static potential conditions, e.g. at 1.5 V vs. NHE, a decrease of the electrode potential to any value above 1.0 V does not lead to a change of the degree of surface coverage, as it is evident from the Figure 7 [2].

A hysteresis of the surface coverage is evident up to the potential values up to approx. 1 V. Hysteresis is not observed at the potential values below 1 V. At the potential values below 1.0 V, coulometric measurements confirm that the electrode is far removed from a complete coverage by oxygen. At the potential values above approx. 1.0 V, it is hardly possible to speak of the Pt surface, since the surface is covered by oxides.

The occurrence of a similar situation may be expected in the case of other noble metals with the difference that the potentials corresponding to these changes will be different.

c) Ellipsometry

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Direct investigation of the changes of the Pt surface was made possible only by the recently performed ellipsometric studies. As reported in [2], Reddy, Genshaw, and Bockris used the ellipsometric method for the investigation of the nature of the oxygen film on the Pt electrode in an acid medium. These measurements confirmed that at an electrode potential of approx. 1.0 V, an oxide lattice starts to form at the surface of Pt.

In conjunction with coulometric data, the ellipsometric method made it possible to explain the changes occurring on the Pt surface at the various potentials. The formation of an oxide phase takes place on the surface at the potentials above 1.0 V.

If data are available concerning the nature of the electrode surface and concerning the dependence of the changes of the surface nature as a function of the electrode potential, it is easier to explain why some electrode reactions exhibit considerable rate changes at the potential values corresponding

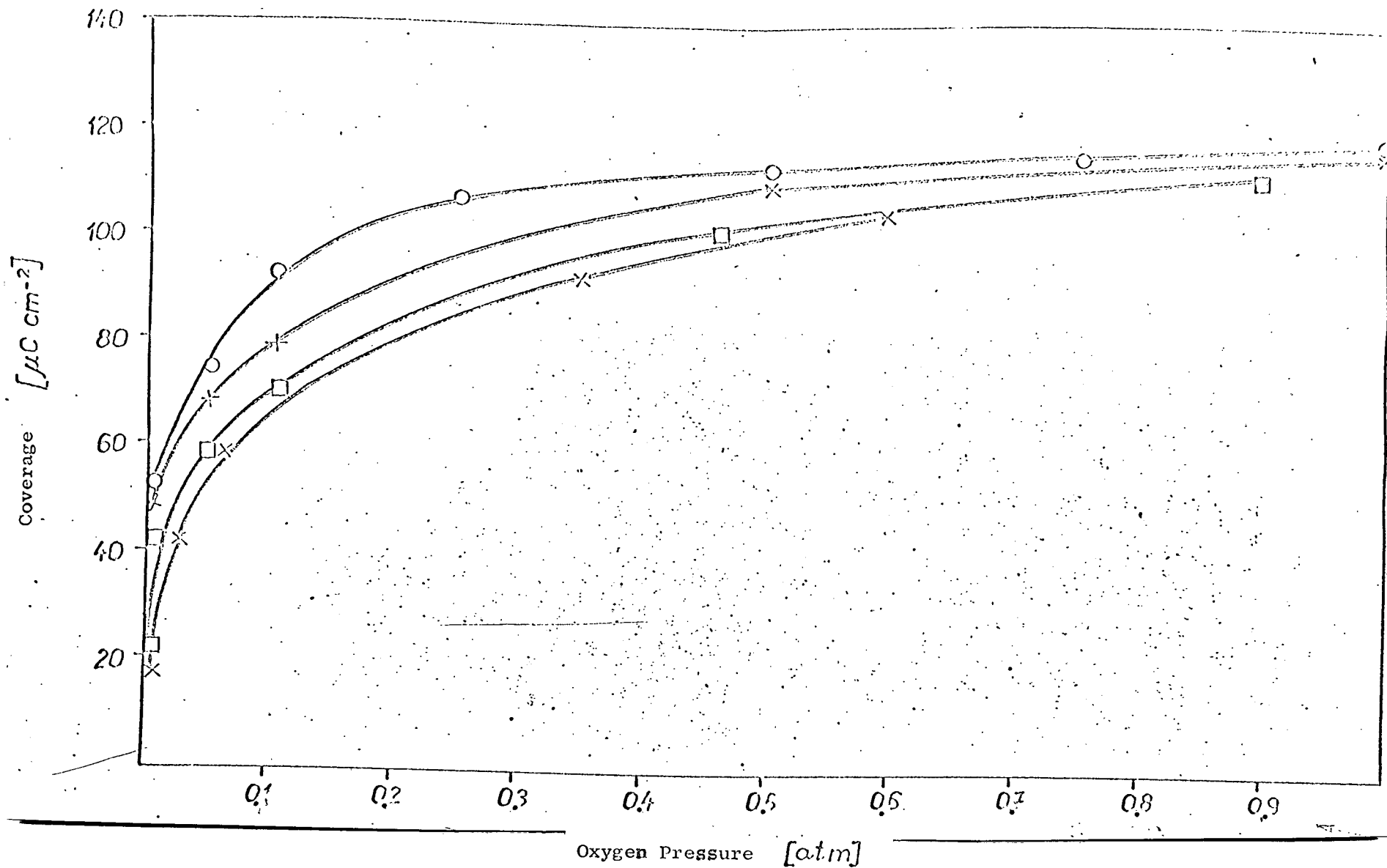


Figure 4. Coverage of pre-reduced Pt electrode held at constant potential in acid medium as a function of oxygen pressure

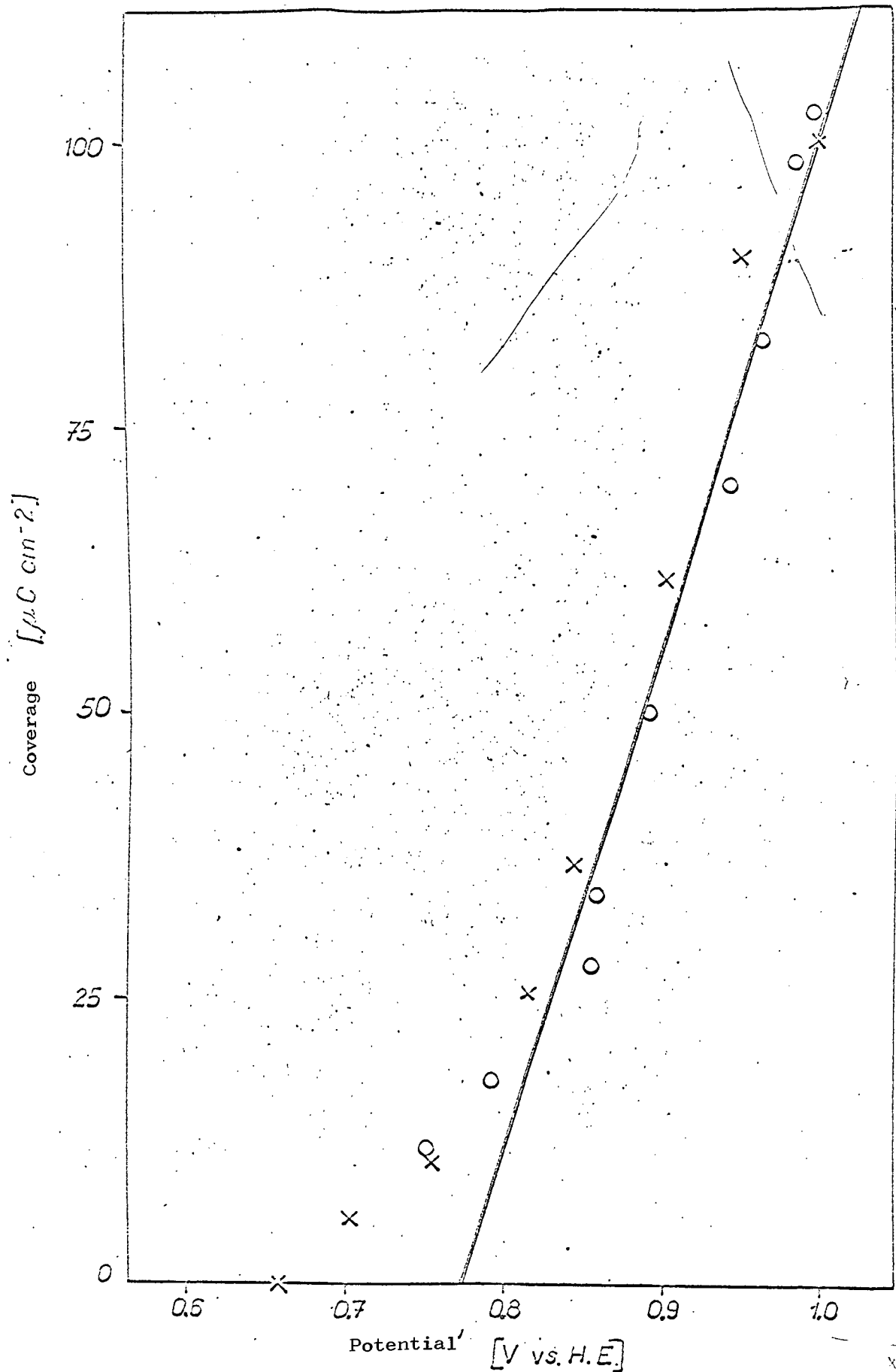


Figure 5. Dependence of coverage on electrode potential [2].

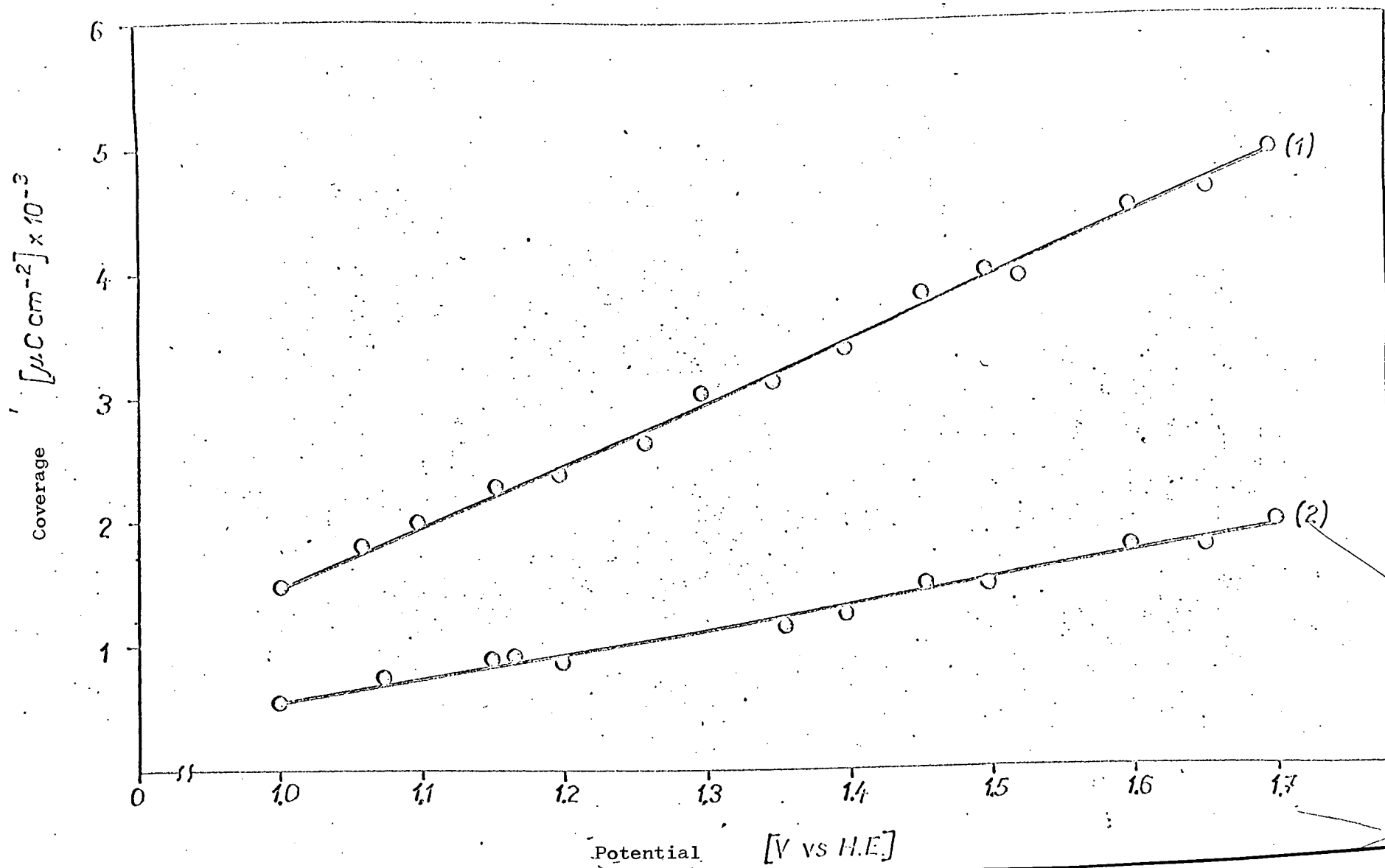


Figure 6. Dependence of coverage on Pt electrode based on coulometric data in the potential range 1.0-1.7 V in acid medium [2].

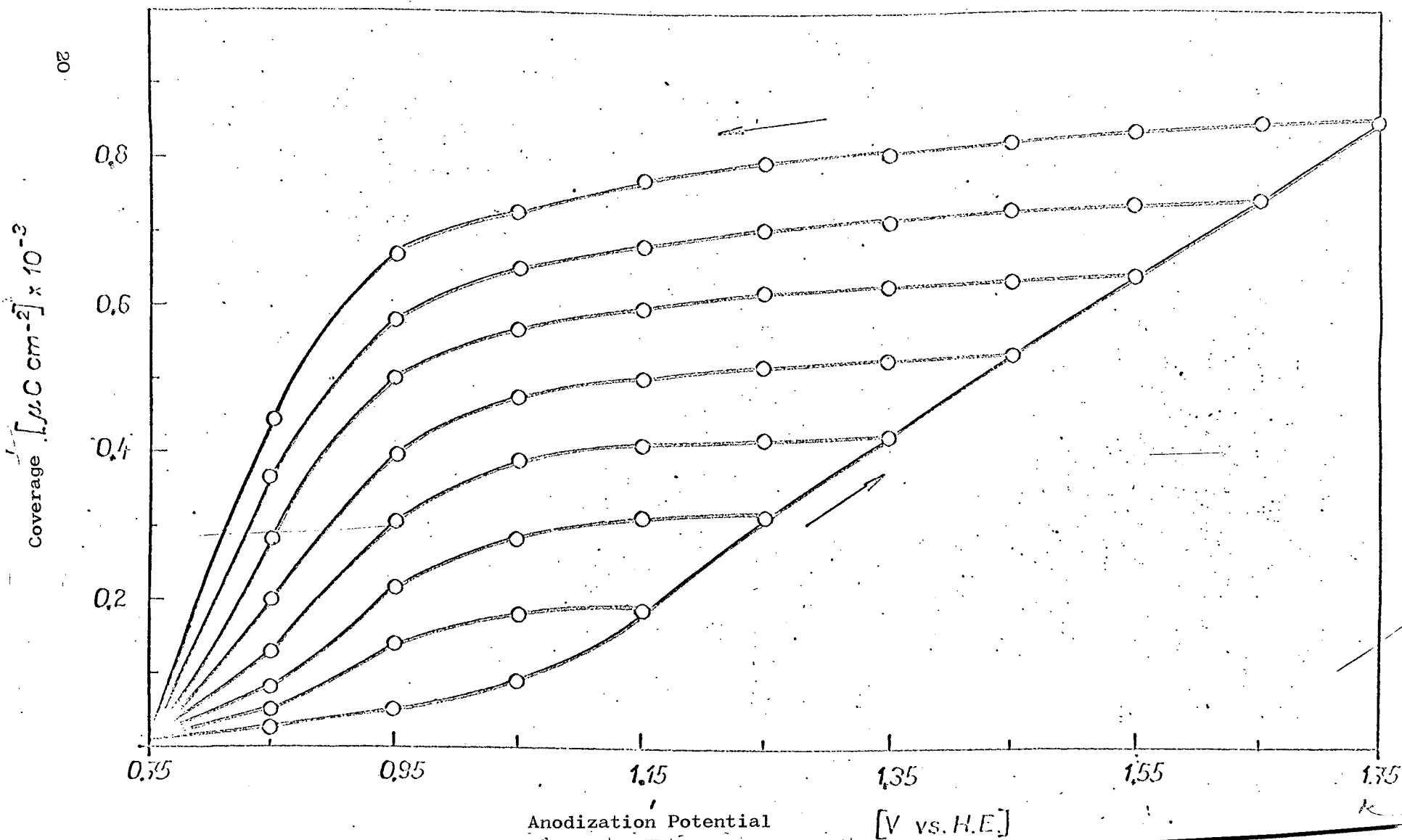


Figure 7. Hysteresis of Pt electrode surface coverage resulting from potential changes [2].

to oxide formation (reduction of oxygen, oxidation of ethylene and of other hydrocarbons).

2.3.2. Surface of Ag Catalysts

/22

It follows from the preceding chapters that the chemical nature of the metal surfaces plays an important role in determining the reaction mechanisms of the events that are occurring at the electrode surface and in conclusively determining the properties of the electrode double layer. It is known that only mercury acts as an uncovered metal in a wide range of potentials, while platinum exhibits a much narrower potential range in which the metal surface is not covered by adsorbed hydrogen or by oxides. Other metals were considerably less investigated and it is impossible to predict if their behavior will resemble that of Hg or Pt.

In the case of silver, the mechanism of the reduction of oxygen as well as measurements at the point of zero charge transfer are complicated by the state of the electrode surface. In practice this depends mainly on the so-called "prehistory" of the electrode. The effect of the state of the silver surface on the electrochemical processes is much more important than previously supposed and mainly in solutions containing alkali metal ions.

Anodic limiting

/23

This phenomenon results from the formation of $[\text{Ag}(\text{OH})_2]^-$ and Ag_2O , as already mentioned in the preceding parts of this communication. Koryta and co-workers [28] studied the behavior of the silver electrode with the aid of cyclic voltammetry in 0.1 M KOH. These authors found that the overall charge transfer during the cathodic polarization in the range 0 to -1200 mV was larger than the anodic charge. The larger cathodic charge was attributed to the formation of a thermodynamically stable thin silver oxide layer on the surface of the electrode. Jansta and Dousek [29] have studied the long-range changes in the electrochemical properties of the hydrophilic oxygen diffusion electrode. These electrodes contained a nickel framework and a silver catalyst that was prepared by the thermal decomposition of silver oxalate. This investigation was carried out in 7 N KOH. The observed decrease of the activity of these electrodes was attributed by these authors to the possible formation of stable

oxide films at the silver surface. These films may form a passivating layer on the electrode which then acts as an inhibitor of the reduction of oxygen.

It is doubtful if in the above-mentioned cases the formation of silver oxides was the cause of the observed phenomena, since, as it was mentioned in the preceding parts of this communication Section 2.2 and, above all in the paper of Giles et al. [19] the Ag_2O monolayer is stable only at the potential which is more negative by 8 mV than the reversible potential $\text{Ag}/\text{Ag}_2\text{O}$ ($E_0 = + 0.342 \text{ V}$).

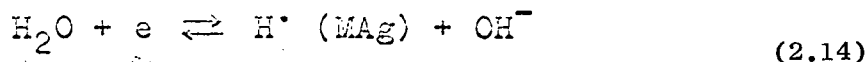
Cathodic limiting

This phenomenon results from the cathodic deposition of the alkali metal and the evolution of hydrogen, the degree of reversibility of the alkali metal deposition being undefined at present. Giles and Harrison [3] studied the behavior of the 111 silver monocrystal electrodes in alkaline solutions by determining the impedance with the aid of Wien's alternating bridge and cyclic voltammetry in the so-called double-layer region. The decision to use these methods was based on the literature data which are in part briefly summarized below.

Kabanov and coworkers [39, 40, 41, 42] proved in 1968 that the alkali metal is incorporated into some metallic cathodes. In subsequent investigations, these authors found that the hydrogen overvoltage in alkaline solution is, especially in the case of silver, time dependent and that the slope of Tafel's plot increases with cathodic polarization, especially if this polarization is more negative than -1.75 V . At a constant current density, the ultimate hydrogen overvoltage value increases with the increasing ionic diameter of the alkali metals in the order $\text{Li} < \text{Na} < \text{K} < \text{Cs} < (\text{CH}_3)_4\text{N}^+$. It was confirmed that the oxidation of alkali metals at the electrode surface is retarded by the preferential formation of intermetallic compounds of the metal-silver type. /24

Zhutayeva [43, 44, 45] carried out measurements using cyclic voltammetry and the results achieved confirmed that, during cathodic polarization, hydrogen and the alkali metal are evolved at the electrode simultaneously and the alkali metal forms an intermetallic compound with silver at the same time.

Giles and Harrison [30] have shown that the potential values near -50 mV (vs. $\text{Ag}_2\text{O}/\text{Ag}$) generate either the dissolution of silver with the formation of $[\text{Ag}(\text{OH})_2]^-$ or the recurrence of the deposition of the metal, depending on the anodic or cathodic behavior of the electrode. Further measurements showed that in the potential range from -50 to -1640 mV (vs. $\text{Ag}_2\text{O}/\text{Ag}$) other Faradaic processes take place. It is probable that up to a potential of -1050 mV the evolution of hydrogen atoms (H^\bullet) takes place at the silver-alkali metal surface when the electrode is used as a cathode. On reversal of the polarity, these hydrogen atoms leave the electrode according to the equation



where M is the alkali metal atom. The deposition of alkali metal at the preferred locations of the silver surface occurs simultaneously with the formation of the MAg surface phase according to the equation



and the concurrent formation of hydrogen ions according to Eq. (2.14).

At the negative potential above -1050 mV, further deposition of alkali metal takes place at the less preferred locations and the Ag electrode becomes completely covered by the alkali metal atoms.

The extended action of negative potentials of -1300 mV, or higher, produces the deposition and concurrent dissolution of the alkali metal at the silver surface which leads to the surface recrystallization and the corresponding increase of the preferred sites for the deposition of the alkali metal M.

From the above experiments it was concluded that the evolution of the alkali metal and hydrogen clearly retards the rates of reduction of oxygen and of hydrogen peroxide. Measurements showed that at the potential of -1080 mV (vs. $\text{Ag}_2\text{O}/\text{Ag}$) the deposition of alkali metal takes place at the surface of the monocrystalline silver electrode and that it is not reoxidized readily at the surface. For these reasons, kinetic measurements may be performed on the bare surfaces of the silver electrode only in the potential range between -100 and -900 mV (vs. $\text{Ag}_2\text{O}/\text{Ag}$) in 1 M solutions of the alkali metals. /25

2.2.4. Adsorption of ions.

The electric double layer and the adsorption of ions in this double layer play important roles in electrochemistry. It is very useful to have the information concerning the nature of the double layer and concerning the quantity of ions adsorbed in this layer. Until very recently, only very few convenient methods were available for the study of ionic adsorption. None of these methods, however, could be applied to the determination of ionic adsorption on a solid metal.

Bockris [31] developed a new ellipsometric method for the study of ionic adsorption in 1967. This development was necessary because the radioisotope method previously developed by Soviet chemists was limited by the availability of the radioactive isotopes and their low concentration. The other methods that were previously used also suffered from specific limitations.

The electrocapillary method gives satisfactory results in determining the quantity of the adsorbed ions on a liquid metal, but is unsuitable for the study of ionic adsorption on solid metals.

The ellipsometric method was first used in the study of the ionic adsorption on mercury and the results obtained were compared with the data obtained from electrocapillary measurements. The data obtained from both sources were found to be in a satisfactory agreement. The results confirmed that on increasing the sensitivity of the ellipsometric method it is possible to achieve very satisfactory and reproducible results and the method itself is highly reliable. The groundwork for the real application of the method to the study of the ionic adsorption on solid metals was laid at the same time.

In the subsequent papers, Bockris [32, 33] continued to report on the development of a general method for the study of ions in the electric double layer. Initially, the adsorption of anions at the surface of mercury was studied with the aid of ellipsometry and the results were compared with the corresponding values obtained by the electrocapillary method. The excellent agreement between the two methods is evident from Figure 8 [32].

Subsequent studies included the following anions adsorbed at the platinum surface: Fluoride, chloride, bromide, iodide, sulfide, and perchlorate. Typical

data for some of the ions are given in the Figures 9 and 10 [32]. The investigation of the ionic adsorption at the Pt surface has further shown that this adsorption may also be irreversible. Investigators therefore started to study the ionic adsorption on the electrodes prepared from various metals by the ellipsometric method. These investigations were aimed at the study of the nature of the bonding forces between the adsorbed ions and the electrode materials. The principal difficulties that arise in the course of these studies are related to the preparation of the electrodes from the various metals in an optically uniform and surface-stable form. The following metals were investigated: gold, silver, rhodium, and nickel. Tin and cadmium electrodes were being prepared. The study included the study of the adsorption of the following anions: chloride, bromide, sulfide, and perchlorate.

2.2.5. Summary

Based on the above-mentioned facts, it is possible to divide the activity of the oxygen electrode with the silver catalyst in strongly alkaline solutions into three basic working regions. These working regions are distinguished by basic changes at the surface of the silver catalyst. These changes depend principally on the potential and the function of the oxygen electrode. Concurrently, these changes are also influenced by the character of the "impurities" in the electrolyte. These working regions are as follows:

a) Working region I

This corresponds to the state of the electrode under load in the primary or the half-cell system in the potential range 0 to -700 mV vs. NHE .

b) Working Region II

This corresponds to the state of the surface of the electrode under load in the potential range from -700 to -1500 mV, or higher vs. NHE. . This working regime may occur under the conditions of the forced electrode polarization, for example, in the half-cell system, or if the O_2 electrode is used as an auxiliary electrode for the supplemental charging of the secondary cells of the type metal-air, or if the polarity of the oxygen electrode is reversed when the cells comprising a battery are wired in series.

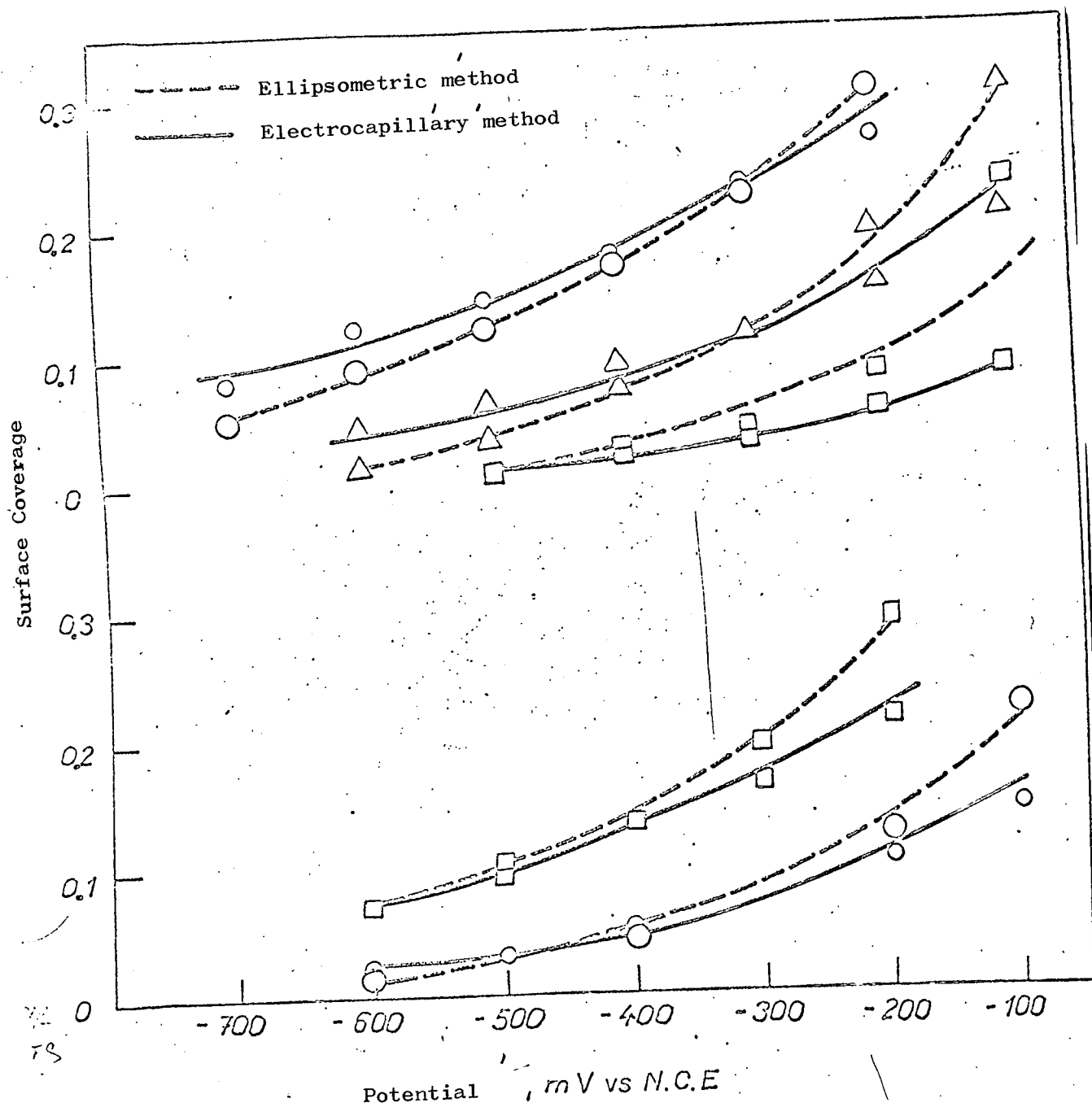


Figure 8. Comparison of the surface coverage data of mercury by KBr solution determined by ellipsometric and electrocapillary methods.[33].

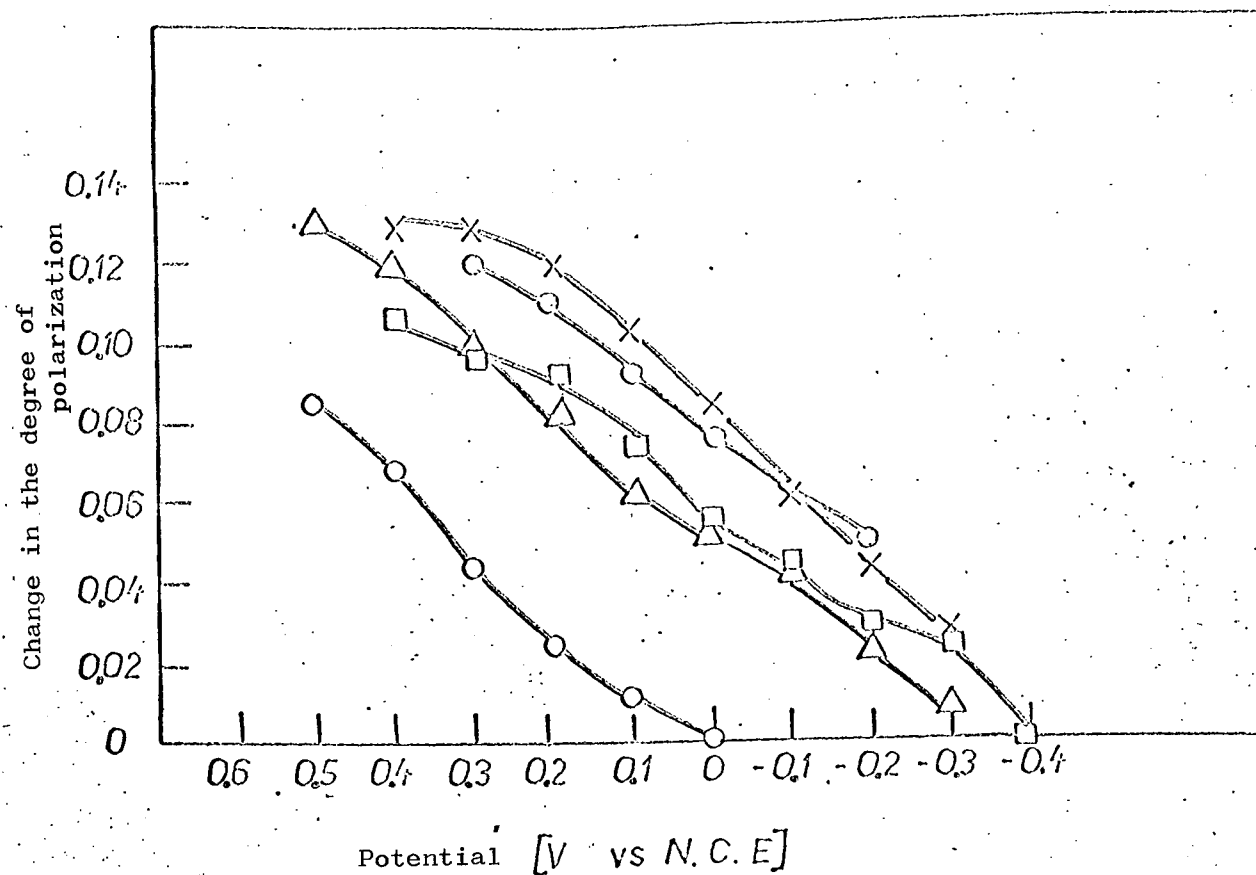


Figure 9. Adsorption Changes (expressed as degrees of polarization) at the platinum electrode surface for NaBr solutions determined by ellipsometric method [33].

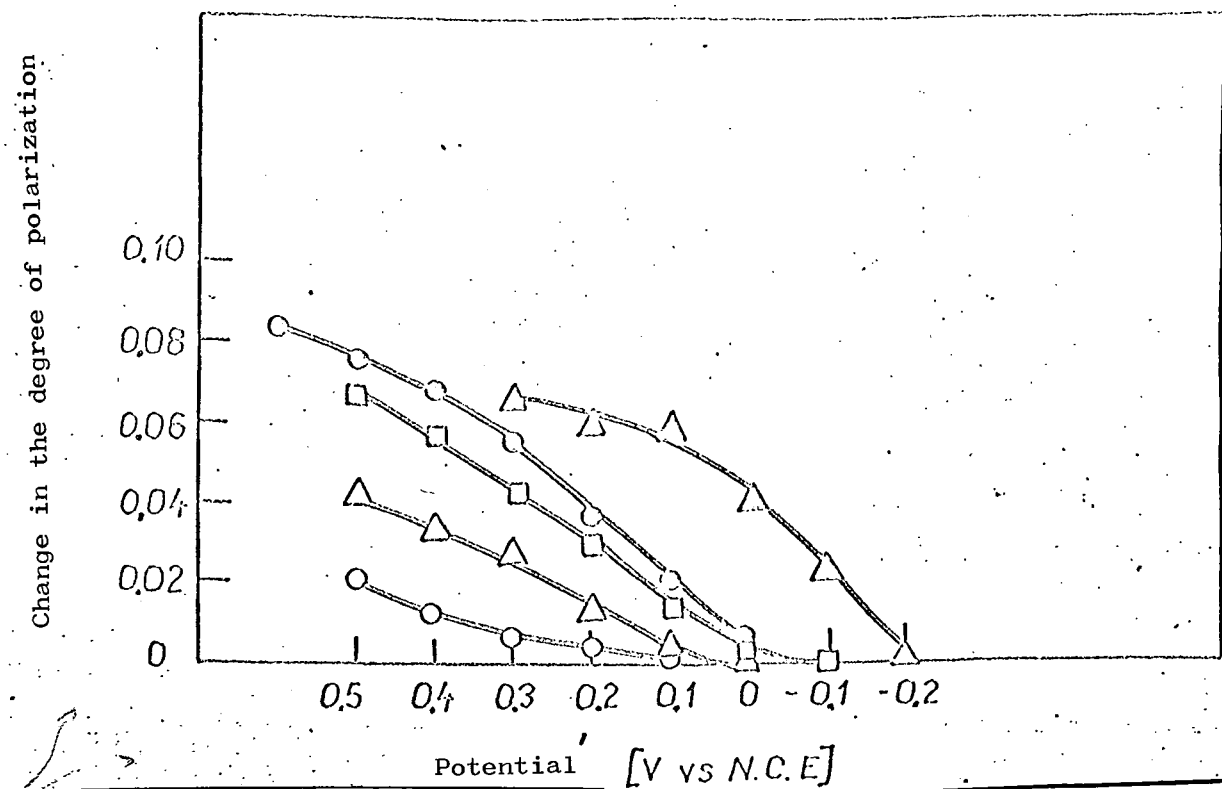


Figure 10. Adsorption changes (expressed as degrees of polarization) at the platinum electrode surface for NaCl solutions determined by ellipsometric method [33].

c) Working region III - zero-load state of the electrode

This corresponds to the zero-load state of the electrode where it is either completely covered by the electrolyte (without oxygen pressure), or remains under the working pressure of oxygen or air. In this case the electrode exhibits the Ag potential in alkaline solution, or the oxygen electrode potential. In both cases, the potential values were in the positive region from /30 +55 to +165 mV vs. Hg/HgO .

The working region I is the most thoroughly investigated region and, since the O₂ electrode works in this region, no appreciable Ag-catalyst activity loss is observed during the long-term electrode activity. The important observation concerning the electrode activity in this region is that the dissolution of Ag takes place in the strongly alkaline medium leading to the formation $[(Ag(OH)_2)]^-$.

The working region II was thoroughly investigated only very recently and the results obtained indicate that it is impossible to assume that the O₂ electrode can work for prolonged periods under the conditions corresponding to this region. Under these conditions, irreversible changes of the Ag surface take place which is reflected in the pronounced decrease of the Ag catalyst activity. This working regime is unusual for this electrode. In the case of the isolated cell it is easy to keep the activity of the O₂ electrode out of this region. In the case of the series wiring of several cells to give a battery, it is very difficult to prevent the occurrence of this state completely. The probable effect of this working region on the activity of the O₂ electrode is illustrated by the fact that, even though the isolated H₂-O₂ fuel cell has a lifetime of 10,000 hours or more, the presently achieved lifetime of battery systems consisting of these cells is approx. 1000 to 3000 hours [3].

The working region III is the least studied region to date. The problem /31 area of concern is principally, whether or not this region has an influence on the lifetime of the electrode containing a silver catalyst in an alkaline solution. The working regime of the O₂ electrode coinciding with this region will be analogous with that of the hybrid fuel cells of the metal-air type working under zero-load conditions. It is evident from the published papers concerning the corrosion of various metals and their alloys that are used as catalysts in O₂ electrodes, as the materials of constructions in cells, and as anode materials

in electrochemical systems, that all these materials are subject to dissolution leading to concurrent formation of complex anions. If, on the other hand, we take into consideration that, under zero-load conditions of the electrochemical system, the most favorable conditions are created for the eventual adsorption of these ions at the surface of the oxygen electrode, it becomes very important from the practical point of view to elucidate the mechanism of the processes occurring in this region and especially to ascertain their influence on the activity loss of the Ag catalyst.

For this reason, the objective of our work was the investigation of this region, since even a negligible quantity of "impurities", such as 10^{-10} mole, can completely cover a 1 cm^2 area of the electrode surface [19].

3. Experimental Part

No convenient experimental method is known to date for following the processes which influence the activity loss of the O_2 electrode, based on a silver catalyst, in alkaline electrolytes under zero-load conditions. This is evident from the content of Section 2.

The only suitable method which could be used for these determinations is ellipsometry, but this technique is not accessible to us at the present time.

For this reason, we chose as the method for the investigation of these processes the relative comparison of the current densities with time.

The results given in the enclosed graphs were obtained by the following technique:

(a) every oxygen electrode to be used for the subsequent determination of the activity loss was polarized for at least 24 hours at the current required to attain an electrode polarization value of -100 to -200 mV vs. Hg/HgO.

(b) After the completion of this step, the V-A characteristic was determined for each electrode. The current density at the potential of -300 mV vs. Hg/HgO was subtracted from this quantity and the resulting quantity was compared with the standard value. /32

We fully realize that this method does not permit an explanation of the nature of the processes occurring at the electrode in the course of its activ-

ity. However, it is possible to elucidate by this method the contribution of the separate effects to the activity loss of the electrode and to identify the effects due to the electrode components as well as those due to the electrolyte components.

3.1. Chemicals Used

Analytically pure chemicals were used for the preparation of the solutions: NaOH, KOH (max. 1.5% CO_3^{2-}), Na_2CO_3 , Ag_2O , ZnO, and HgCl_2 .

Metals

Zn (amalgamated and unamalgamated), Fe, Ni, and Cd were used in powdered form. The materials were analytically pure. The amalgamated zinc contained 14.5% Hg.

Teflon used in the preparation of the oxygen electrode was produced by the French firm Societe Ugine Kuhlmann under the trademark Soreflon 5 in a particle size of $300 \pm 5 \mu\text{m}^*$.

Powdered Ag_2CO_3 was supplied by the n.p.**. Vestec; this material was analytically pure.

AgO was prepared by a chemical method [34].

Preparation of the carbonate-free NaOH solution

The carbonate-free NaOH solution was prepared from a 14.55 N NaOH solution. This concentrated solution was allowed to stand in a refrigerator for 24 hours. The solution was then filtered under exclusion of air through an S 4 fritted disc filter. The filtered solution was diluted with distilled water to a concentration of 7 N KOH. The distilled water used was purged with nitrogen and stored in a polyethylene bottle under exclusion of air in a refrigerator.

Preparation of CO_3^{2-} free 7 N KOH containing dissolved Ag^{I}

This solution was prepared by dissolving 2 g AgO or Ag_2O in 500 ml of 7 N NaOH free of CO_3^{2-} with continuous mixing for 24 hours. On completion of mixing, the solution was filtered through an S 4 fritted disc filter with the exclusion of air. The solution thus obtained was unstable on storage in light.

* Translator's Note: " μm " is meaningless.

** Translator's Note: n.p. = narodni podnik is "people's enterprise."

Preparation of 7 N KOH with dissolved Ag^I

This solution was prepared by dissolving 2 g AgO or Ag₂O in 500 ml of 7 N KOH (containing a maximum of 1.5% K₂CO₃) by a similar method to that given for the preparation of 7 N NaOH containing dissolved Ag^I.

Preparation of K₂ZnO₂ solution.

A weighed-out amount of ZnO is dissolved in a warm KOH solution of a higher concentration (approx. 400 g KOH/100 g H₂O. After dissolution, the mixture is diluted with distilled water to the needed concentration.

3.2. Preparation of the Oxygen Electrode

Catalyst.

The catalyst for the electrochemical oxygen reduction as well as the material for the conducting framework of the electrode was silver obtained by the thermal decomposition of powdered silver oxide (AgO), or of silver carbonate (AgCO₃) in the molded electrode.

Binder,

Powdered polytetrafluoroethylene with a particle size of 300 μ was used as the binder.

Preparation of the mix.

The preparation of Ag₂CO₃ - PTFE (60:40 wt. %) and AgO-PTFE mixes, /34 respectively, was carried out by way of dry homogenization by shaking for approx. 20 minutes.

Molding of the electrode.

The weighed out mixture was poured into the mold and molded under a pressure of 1000 kg/cm² by the following procedure: development of the maximum molding pressure -- 5 minutes, holding period at maximum pressure-- 10 seconds, decompression--4 minutes.

Sintering of the electrode.

The electrode sintering was carried out concurrently with the thermal reduction in an electric oven in air. The electrode was placed between two silver

sheets and sintered for 20 minutes at a temperature of approx. 390°C followed by rapid cooling of the sintered electrode.

On completion of the above-mentioned steps, the electrode was ready for the determination of the polarization, or other properties. These steps were described in more detail in [34]

3.3. Experimental Methods

The determination of the polarization curves, i.e., of the dependence of the electrode potential on the current drawn from the cell, and the current density $E = f(i)$, respectively, was chosen by us as a basic method for the determination of the electrode properties. The measurements were carried out in a half-cell system for gaseous diffusion electrodes. The basic arrangement of this system was described in [35], however for our purposes a more detailed description was furnished in [34] including a description of the recording instruments.

3.4. Experimental Apparatus

The electrode under investigation was, together with the current collector and gasket, placed into a holder. The entire assembly was then placed into a vessel with a Luggin capillary. For long-term measurements, or for the determination of the effect of ambient atmosphere (especially CO₂), it was necessary to close the vessel tightly. We have used the vessel design described in [36] to achieve this purpose. The electrode holder was fabricated from poly(methyl methacrylate).

For the assembly of the electrode holder, bolts fabricated from the following materials were used: Fe, Ni, Cd, Zn, polyamide, polyethylene, polypropylene, and poly (phenylene oxide).

Ag rings and, later, Pt screens were used as the current collectors. The counterelectrode was fabricated from Pt foil or screen. The collector leads were made first from Ag wire, and later, from Pt wire.

Silicone rubber was used as the gasketing material for the electrode in the holder. The measurement vessel was fabricated from glass in the shape of a cylinder which contained a glass stopper with ducts that prevented the access

of CO_2 from the air to the electrolyte. The connection between the stopper and the vessel was formed by a ground joint, the design of the vessel preventing any contact between KOH and the ground glass joint. The measurements were carried out at $63^\circ \pm 3^\circ \text{C}$.

4. Experimental Results

The experimental results represented in the following graphs are expressed as % decrease of the oxygen electrode activity and were calculated according to the equation

$$\frac{\Delta I}{2} = \frac{a - b}{a} \cdot 100 \text{ } [\%] \quad (2.16)$$

where I is the decrease of the activity in %

a is the initial electrode activity in mA/cm^2

b is the activity of the electrode after time t in mA/cm^2

All curves given in these graphs represent the average of a minimum of 3 and of a maximum of 10 samples. The measurements of the rate of activity loss with time were carried out at the temperature of $63 \pm 3^\circ \text{C}$ mostly in the zero-load state with the electrode completely immersed.

4.1. Effect of Ag^I on the Lowering of the O_2 Electrode Activity Under Zero-Load Conditions with and without O_2 Pressure

/36

The experiments of this series show that the deactivation of the oxygen electrode under zero load is more clear-cut when the electrode is completely immersed into the electrolyte than in the case of incomplete immersion (without O_2 pressure). In both cases, Ag^I present in the form of the soluble anions goes into the electrolyte during the experiment. This fact was observed in the case of NaOH as well as of KOH as the electrolytes. The ratio of the lowering of the oxygen electrode activity under zero load with and without O_2 pressure is 1:2.5, as it is seen from Figure 11.

In the case of Ag^I being present at the beginning of the experiment in the form of the anion $[\text{Ag}(\text{OH})_2]^-$ arising from the dissolution of Ag_2O in KOH or NaOH, a substantial part of the activity lowering of the oxygen electrode under zero load is already observed during the stage when the electrode is under the working pressure of oxygen. The ratio of the lowering of the oxygen electrode

activity under these conditions, i.e., without and with oxygen pressure is then 1:1.5, as it is seen from Figure 12.

We have further determined the effect of the Ag collector on the O_2 electrode and of the Ag leads connected to this connector and to the auxiliary Pt electrode on the activity lowering of the oxygen electrode at zero load and with complete immersion of the electrode, i.e., without O_2 pressure. In this case, the most favorable conditions are created for the lowering of the activity, especially on a long-term basis.

From the curves in Figure 13, it is seen that the silver collector on the oxygen electrode and the silver leads connected to this collector and to the auxiliary electrode have the same negative effect on the activity lowering of this electrode as the effect of the presence of Ag^I in the electrolyte in the form of an anion at the start of the experiment.

It follows from Figures 11, 12, and 13 that the O_2 electrode consisting of Ag catalyst-macromolecular material, placed into a strongly alkaline medium, exhibits a spontaneous decrease of the activity due to the influence of its own catalyst which dissolves in the electrolyte as Ag^I in the form of complex anions during the functioning of the electrode. This occurs when the electrode is operated under zero load under the working pressure of oxygen as well as in the case of the complete immersion into the electrolyte.

The fact that the concentration of Ag^I in 7 N KOH ($4.8 \cdot 10^{-4}$ N) present in the form $[Ag(OH)_2]^-$ may eventually cause a lowering of the O_2 activity of the Ag electrode containing silver catalyst can be demonstrated by an experiment of the opposite character. The two-component porous Zn/PTFE electrode, prepared by a technology similar to that used to prepare the Ag electrodes, was kept in the completely immersed state under zero load for about 90 hours in 7 N KOH electrolyte solution which was saturated with dissolved Ag^I in the form of the anion $[Ag(OH)_2]^-$ at ambient laboratory temperature. After the indicated time span, this electrode was exposed to the working pressure of O_2 and the potential of this electrode was measured over a period of 60 hours. These results are pictured in Figure 14. From the final values of the potential of this electrode exhibited the same potential as that of the normal oxygen elec-

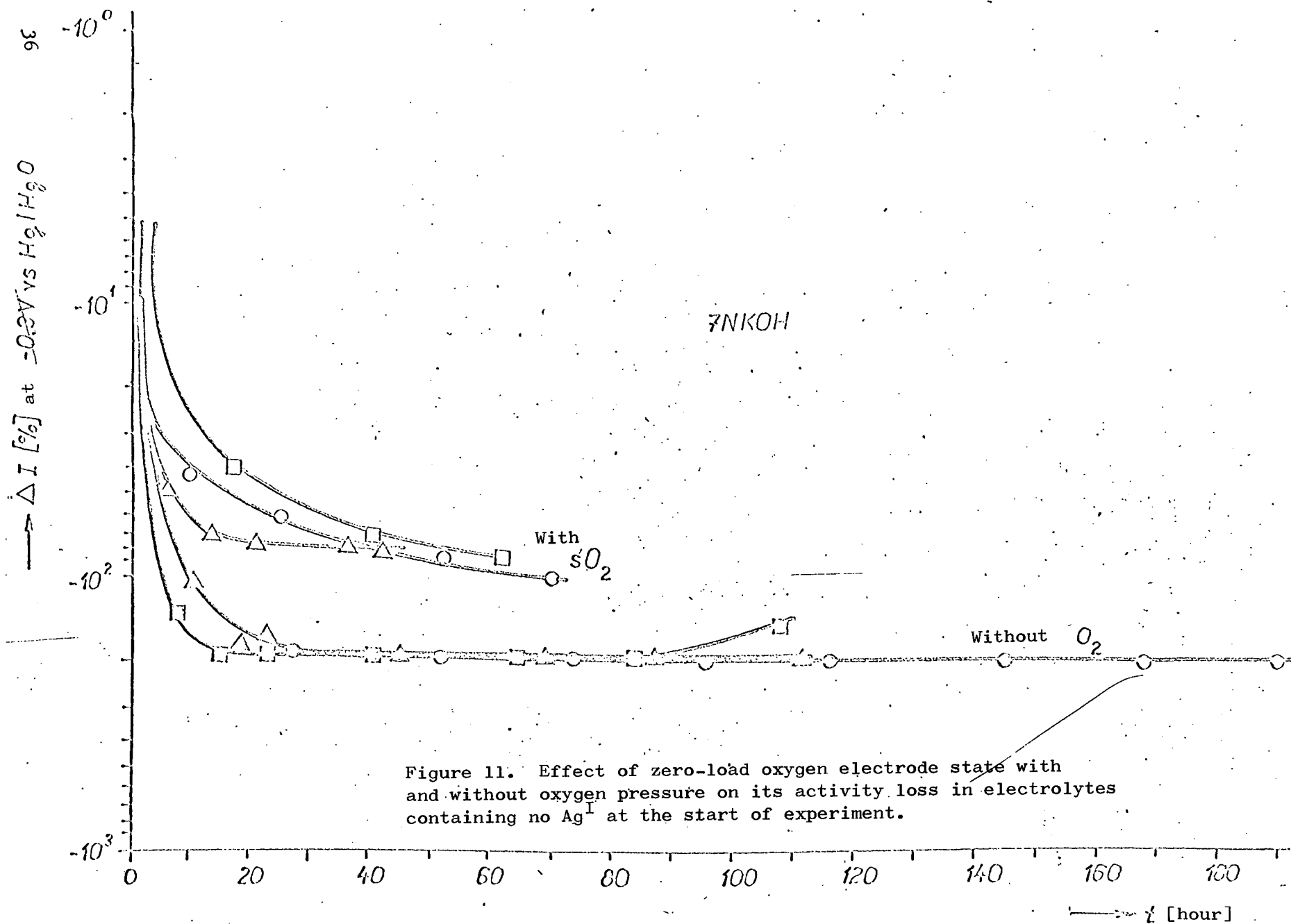


Figure 11. Effect of zero-load oxygen electrode state with and without oxygen pressure on its activity loss in electrolytes containing no Ag^+ at the start of experiment.

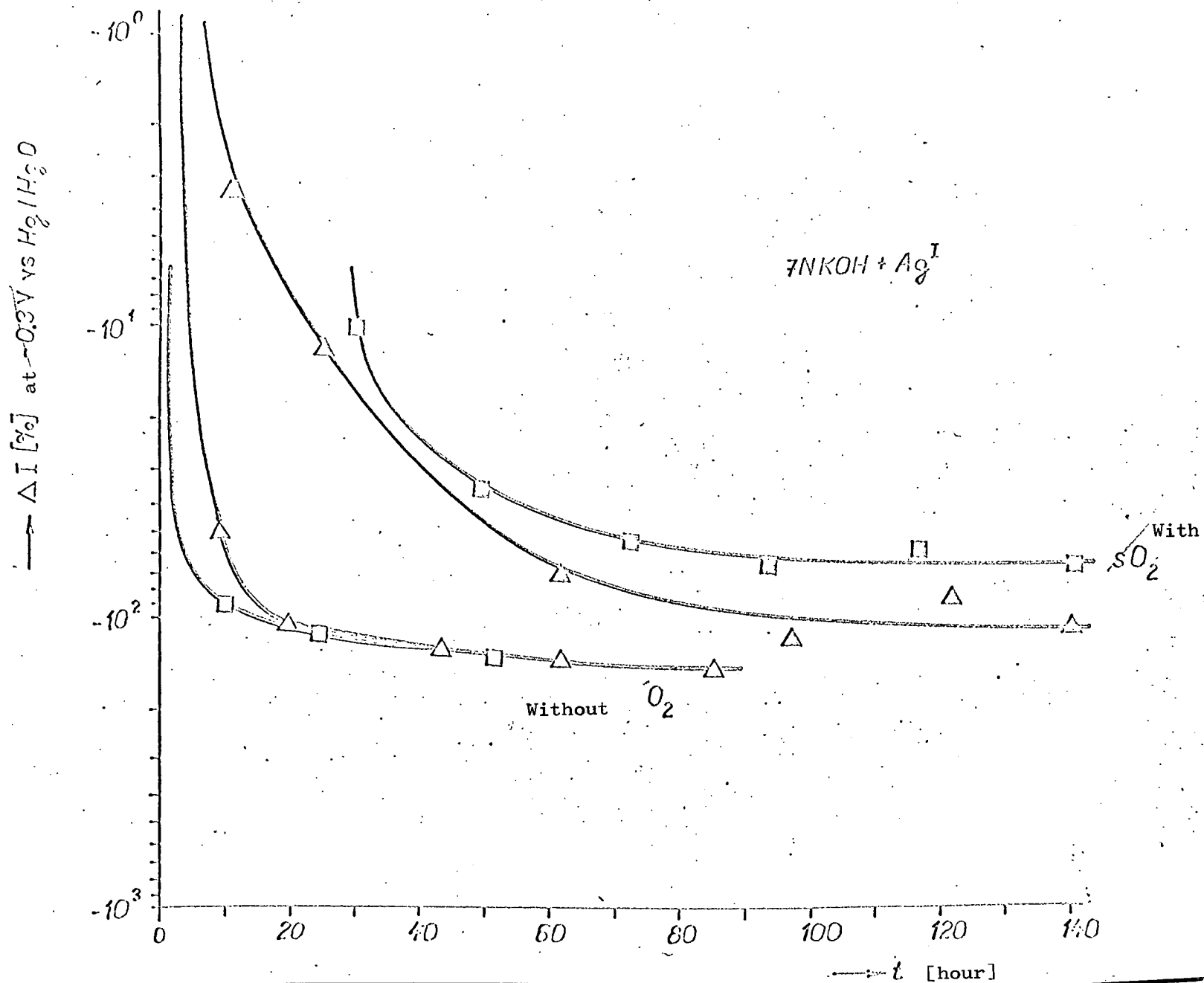


Figure 12. Effect of zero-load oxygen electrode state with and without oxygen pressure on its activity loss in electrolytes containing Ag^{I} at the start of the experiment.

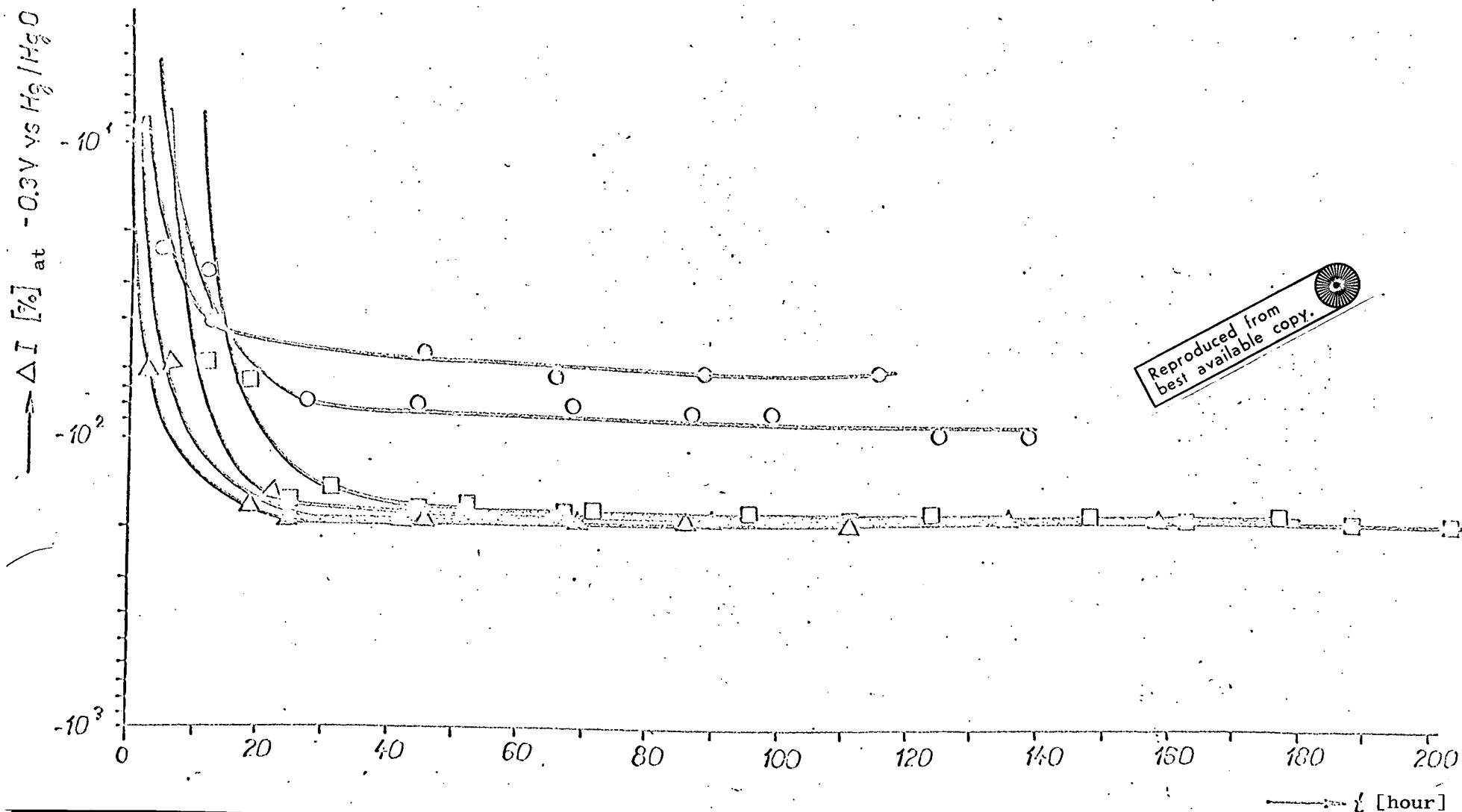


Figure 13. Effect of Ag collectors and leads on lowering of the electrode activity under zero load and with complete immersion.

trode under investigation, even when at the start of the experiment its potential was the same as that of the Zn electrode. The same value of the potential was observed when the electrode was not under oxygen pressure. The electrode based on the zinc framework, and exposed to the above-mentioned conditions, was also evaluated in terms of its usefulness as an oxygen electrode, i.e. with polarization. This electrode could carry a load corresponding to the current density of $1-2 \text{ mA/cm}^2$ at a polarization of $-300 \text{ mV vs. Hg/HgO}$ for a period of about 60 hours. Oxygen electrodes which were subject to the activity decrease with time showed similar levels of current density. /40

4.2. Effect of Polarization on the lowering of the O_2 Electrode Activity

This effect was investigated in each experiment when the oxygen electrode was under zero load and the following observations were made:

The decrease of the oxygen electrode activity under load with time is approx. 6 times smaller than that observed in the case of the same electrode exposed to the same conditions without oxygen pressure and at zero load.

The effect of the polarization of the oxygen electrode was investigated in the potential range from -150 to -200 mV , measured at $-300 \text{ mV vs. Hg/HgO}$ and it was found that the decrease of the activity is about 35% from the "original values". The different effects in the case of the polarization of the oxygen electrode and in the case of its state without oxygen pressure may be seen in Figure 15.

It is possible to state that the activity decrease of the oxygen electrode catalyst depends mainly on the potential of this electrode in a way that with increasing positive potential of the oxygen electrode (vs. Hg/HgO) the loss of the electrode activity increases.

The activity of the oxygen electrode was not affected by using 7 N KOH instead of 7 N NaOH. /42

4.3. Effect of Zn, Ni, Fe, and Cd on the Lowering of O_2 Electrode Activity

In addition to the determination of the activity decrease of the oxygen electrode proper, it is necessary to know the influence of other metals that

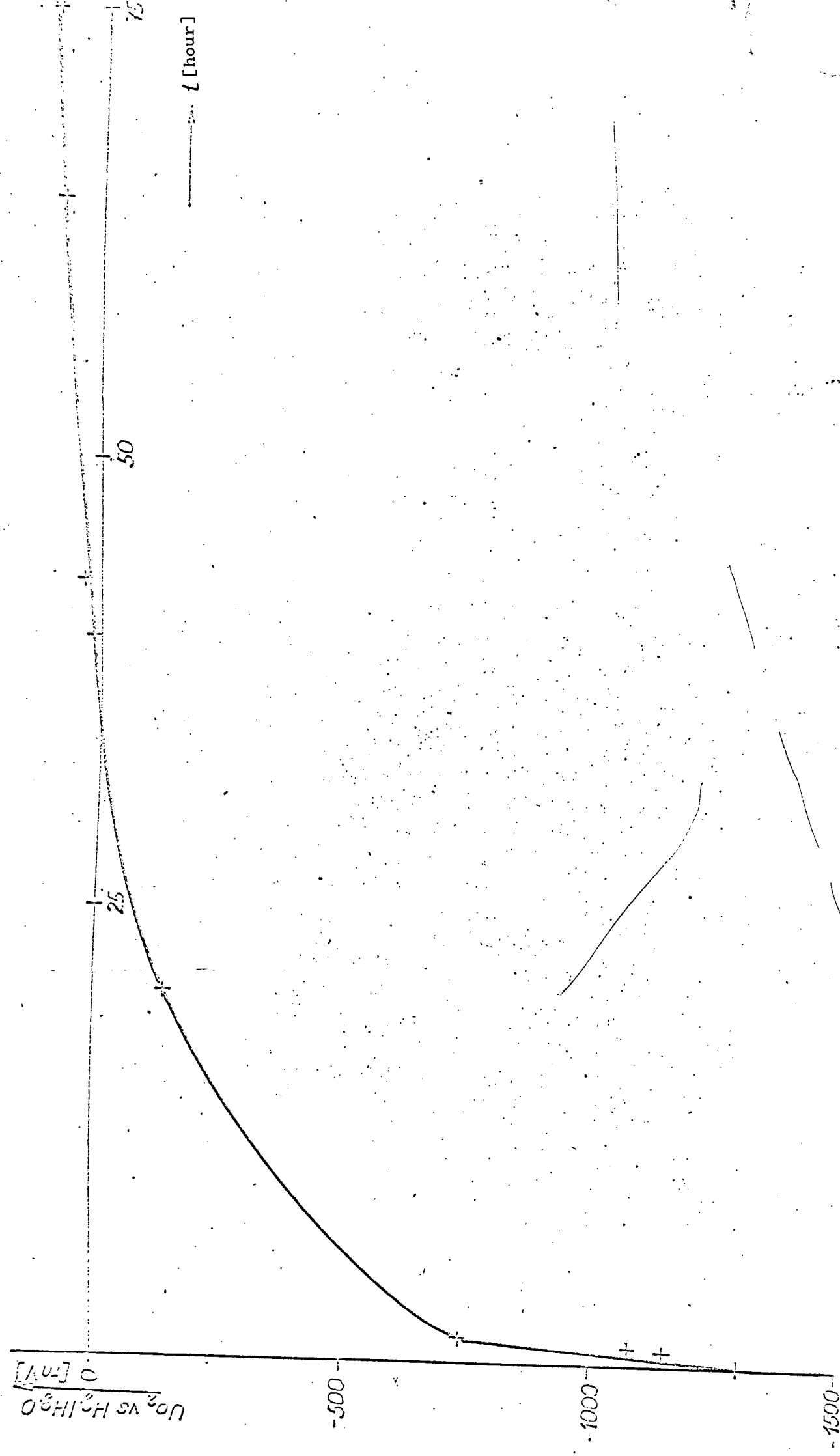


Figure 14. Change of Zn-PTFE electrode potential under the influence of Ag^{I} present in $[\text{Ag}(\text{OH})_2]^-$ in 7 N KOH electrode in $4.8 \cdot 10^{-4}$ N concentration.

may be present either as the anode material, for example Zn or Cd, or as the ^{/44} fuel cell construction material (for example, Ni, Fe, etc.) on the performance of the O₂ electrode. The elucidation of the effect of these metals is especially important due to the fact that these metals may even in small concentrations dissolve in the 7 N NaOH or KOH electrolyte by a corrosion mechanism [cf. Section 2.2].

The results obtained during the elucidation of the effect of Cd, Ni, and Fe on the O₂ electrode at zero load and without O₂ pressure are given in Table II and graphically represented in Figure 16. The above-mentioned metals were added to the electrolyte in powdered form in the quantities of 0.5 g per experiment. The results obtained show that these metals somewhat decrease the activity

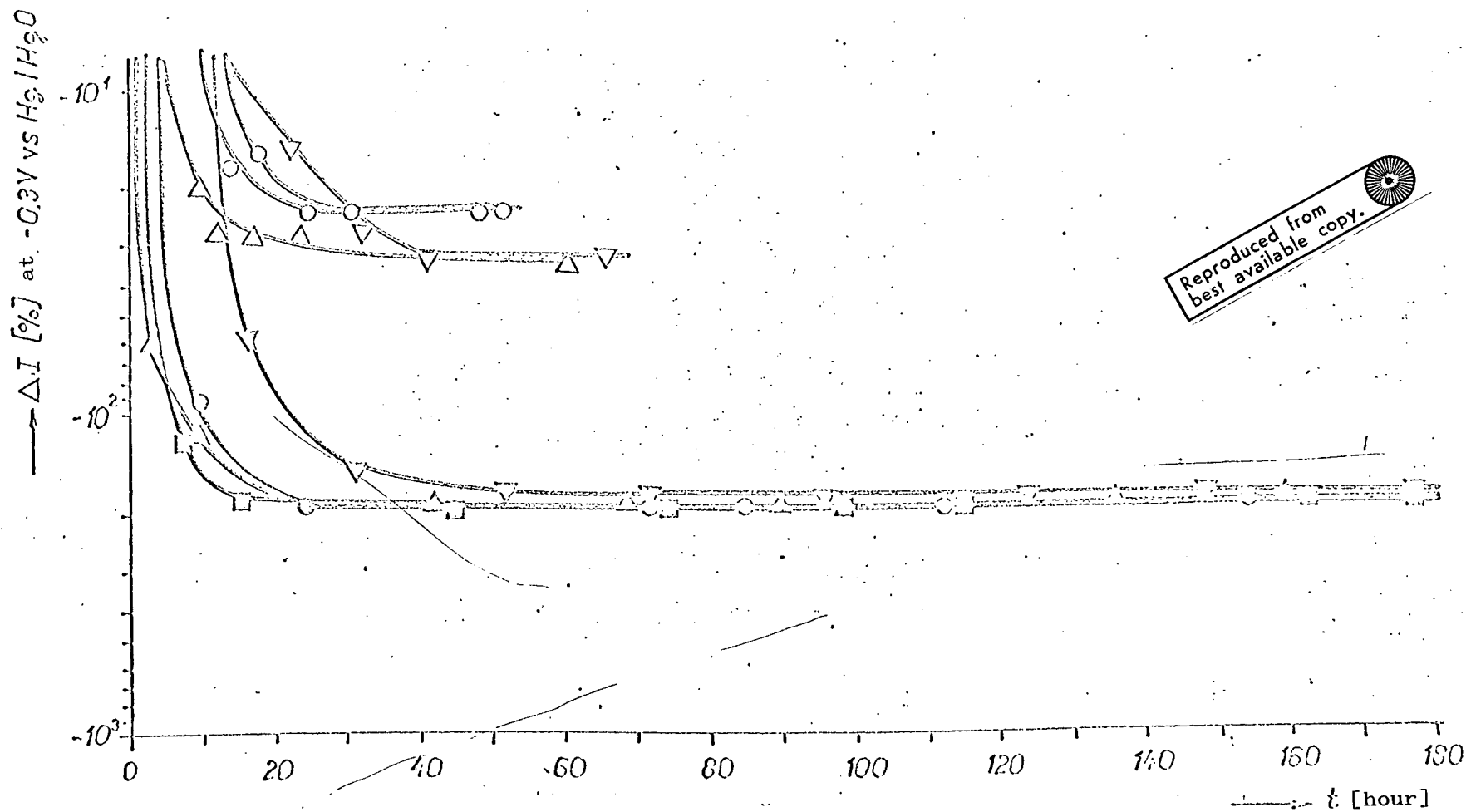
TABLE II. DECREASE OF THE ACTIVITY OF THE OXYGEN ELECTRODE UNDER THE INFLUENCE OF Fe, Cd, Ni, AND Zn AFTER 120 HOURS OF OPERATION UNDER ZERO LOAD WITHOUT OXYGEN PRESSURE

Nature of Additive	Loss of Activity of the Oxygen Electrode I/2 %
Without additives	99
Fe	96
Cd	90
Zn	22
Fe+Zn	77
Amalgated Zn	83

loss of the original oxygen electrode caused by the argentate anions. This observation is probably due to the possible deposition of Ag at the surface of these metals because of the potential differences between Ag and the other metals, i.e. due to the so-called cementation. This fact is especially evident in the case of Zn which is also confirmed in [37 and 38].

The order of the positive action of the metals used on the decrease of the activity loss of the O₂ electrode is as follows: Zn > Ni > Cd > Fe.

It was established at the same time that the soluble ions of these metals have neither a positive, nor a negative effect on the performance of the O₂ electrode during its polarization as well as in the zero-load state without oxygen pressure. The negative influence of the soluble Cd, Ni, and Fe ions



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Figure 15. Effect of polarization and zero load without oxygen pressure on activity decrease of oxygen electrode.

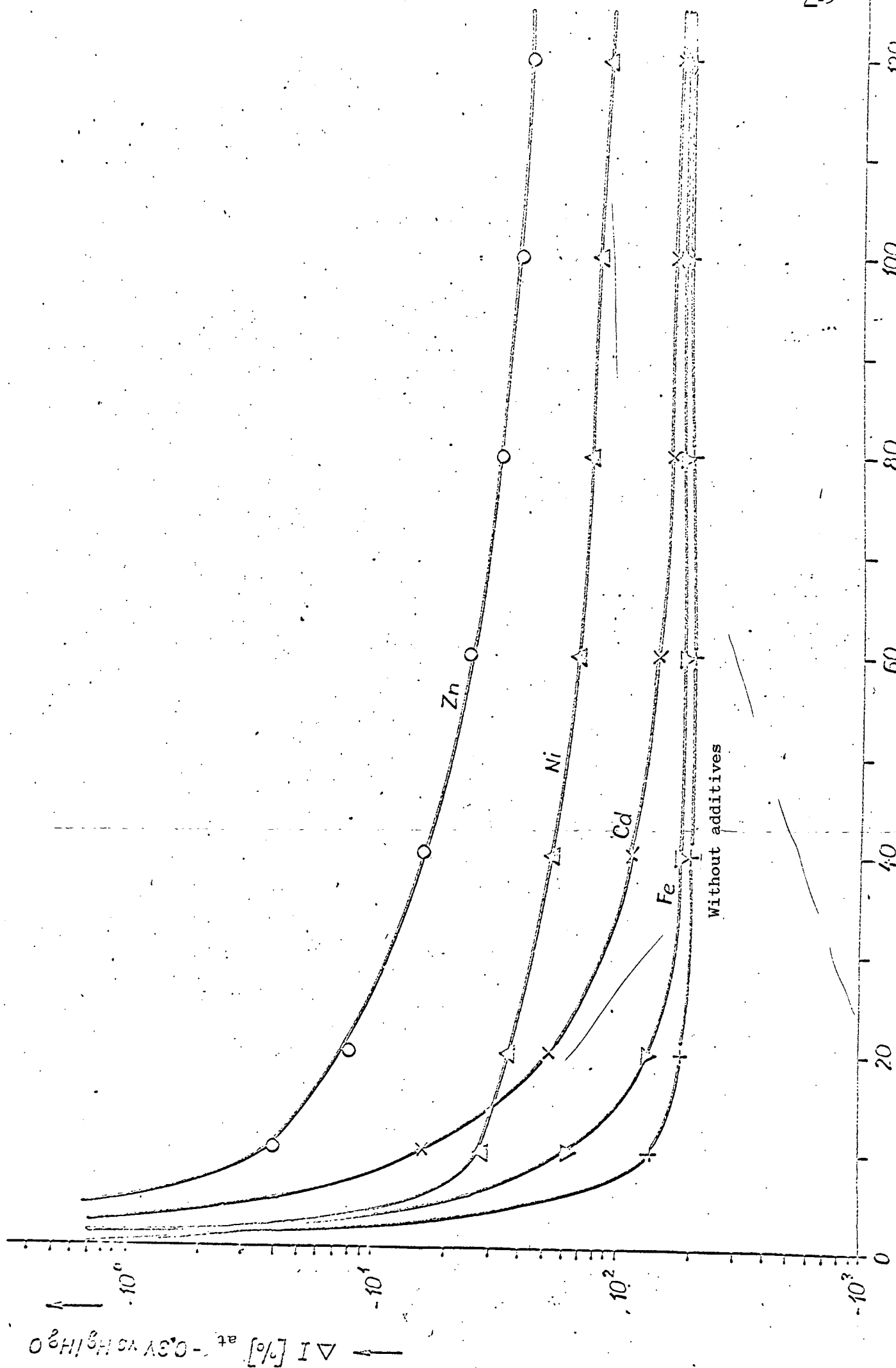


Figure 16. Effect of Zn, Cd, and Fe on the oxygen electrode zero-load state without oxygen pressure.

is evidently undetectable because of the dominant negative influence of Ag^{I} which is present in the form $[\text{Ag}(\text{OH})_2]^-$.

4.4. Effect of Amalgamation on the Lowering of O_2 Electrode Activity

The effect of the amalgamation (with the 2.5% HgCl_2 solution) on the activity decrease of the oxygen electrode without oxygen pressure was determined under zero-load conditions. The results represented in Figure 17 show that this amalgamation did not influence the electrode activity in a detectable way.

4.5. Retarding Effect of Zn on the Lowering of O_2 Electrode Activity

It is seen from the curves shown in Figure 18 and the data listed in Table II that metallic zinc exhibits the strongest influence on the retardation of the activity decrease of the oxygen electrode under zero-load conditions without O_2 pressure. Zn was added to the electrolyte in powdered form in quantities of 5 g per experiment, which quantity is substantially larger than those of added Ni, Cd, and Fe. The reason for the substantially larger amount of added Zn is the considerably greater corrosion intensity in the electrolytes used and at the working temperatures employed. An analogous positive effect of Zn on the retardation of the activity decrease of the O_2 electrode was observed in the presence of powdered Fe, as it is evident from the curves in Figure 19. It was also found that the presence of Zn in the zincate form has no effect on the activity drop of the O_2 electrode. The positive effect of Zn on the retardation of the activity decrease of the O_2 electrode under zero-load and without oxygen pressure may be explained by the capability of metallic Zn to deposit Ag from the anionic form $[\text{Ag}(\text{OH})_2]^-$ on its surface as it was pointed out in [37 and 38].

It follows from the curves in Figure 18 that the positive effect of Zn is substantially lower when zinc is used in the amalgam form (the actually used material contained 14.5% Hg).

4.6. Effect of CO_3^{2-} on the Performance of the Oxygen Electrode.

The investigation of the effect of CO_3^{2-} was carried out in 7 N NaOH. During the operation under load, the activity of the O_2 electrode is lowered

by increasing the carbonate concentration in the NaOH solution, as indicated by the data in Figure 20. In the case of the O_2 electrode operation under zero-load conditions and without O_2 pressure, the presence of carbonate has a positive effect up to the concentrations up to 9.5% CO_3^{2-} . The positive effect was no longer observed in the presence of 19.5% CO_3^{2-} .

It follows from the above-mentioned facts that, even though carbonates /50 retard the activity drop of the O_2 electrode under zero-load conditions without O_2 pressure, their presence is undesirable, especially when the electrode is under load.

4.7. Working Pressure of the Oxygen Electrode

In the course of the preparation and testing of the fabricated oxygen electrodes, it was found that the molding regime has a substantial influence on the working pressure of these electrodes. Our objective was to achieve electrodes operating in the low-pressure regime, i.e. at the pressures below 50 cm water column. The molding conditions were not optimized, but the production of the electrodes operating in the low-pressure range of 14 \pm 4 cm H_2O column proved to be very reproducible as long as the molding regime given in Section 3.2 was maintained.

4.8. Sintering Temperature of the Oxygen Electrode.

It is evident from the measurements obtained that the performance of the oxygen electrode is substantially influenced by the sintering temperature. The optimum value of this temperature will be different for every batch of Ag_2O prepared until it is possible to insure that the various batches of prepared Ag_2O have the same physical and chemical properties [13]. A similar situation may also be expected in the case of Ag_2CO_3 .

5. Conclusions

From the results given in Section 4 it is evident that the zero-load state of the oxygen electrode consisting of a silver catalyst and PTFE and operating either in the presence or in the absence of oxygen (air) causes a time-dependent decrease of the silver catalyst activity to the point that the oxygen electrode of this composition is practically useless for the purposes of application in electrochemical systems from the point of view of the demonstrated performance.

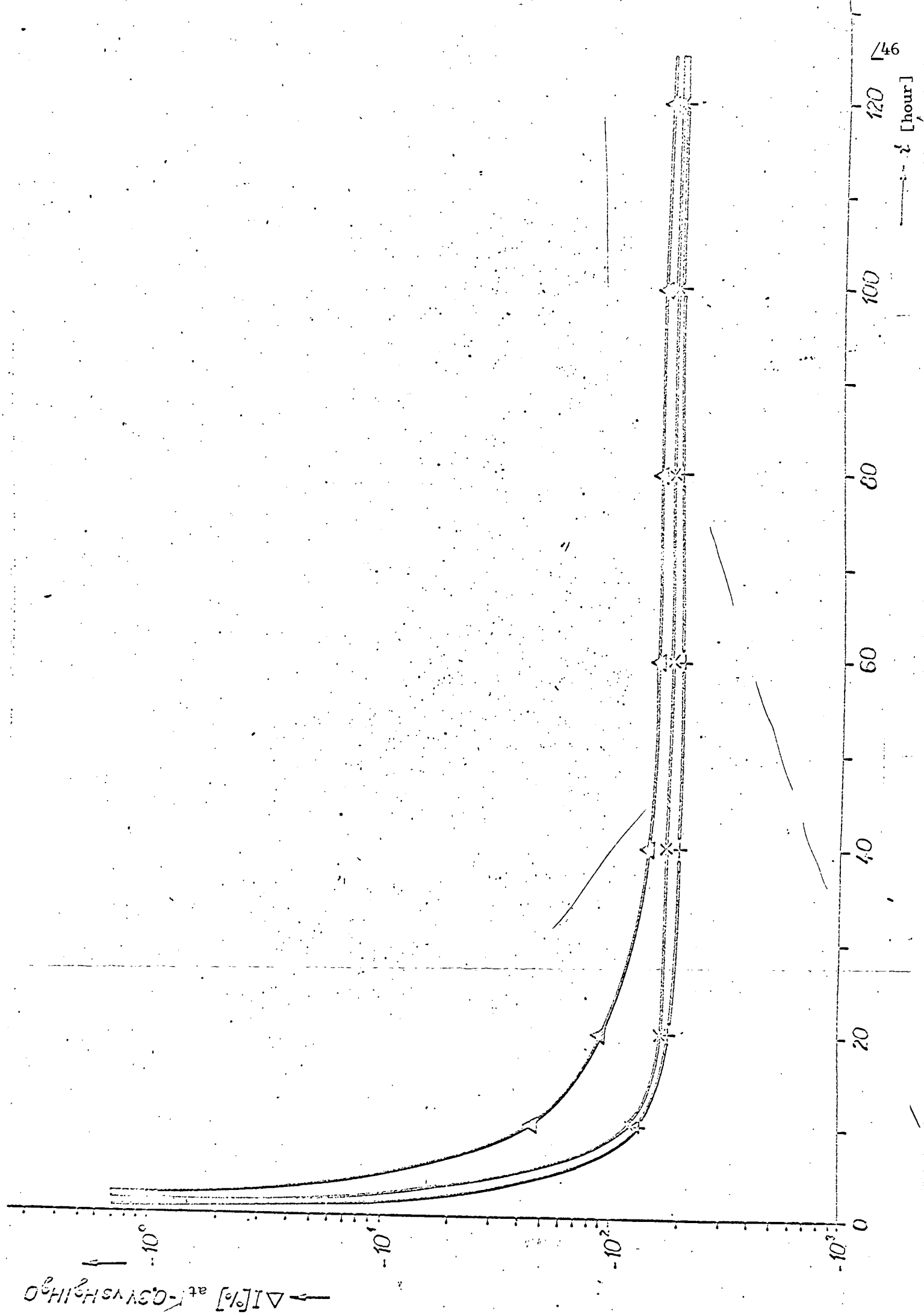


Figure 17. Effect of oxygen electrode amalgamation on its activity decrease without oxygen pressure under zero-load conditions.

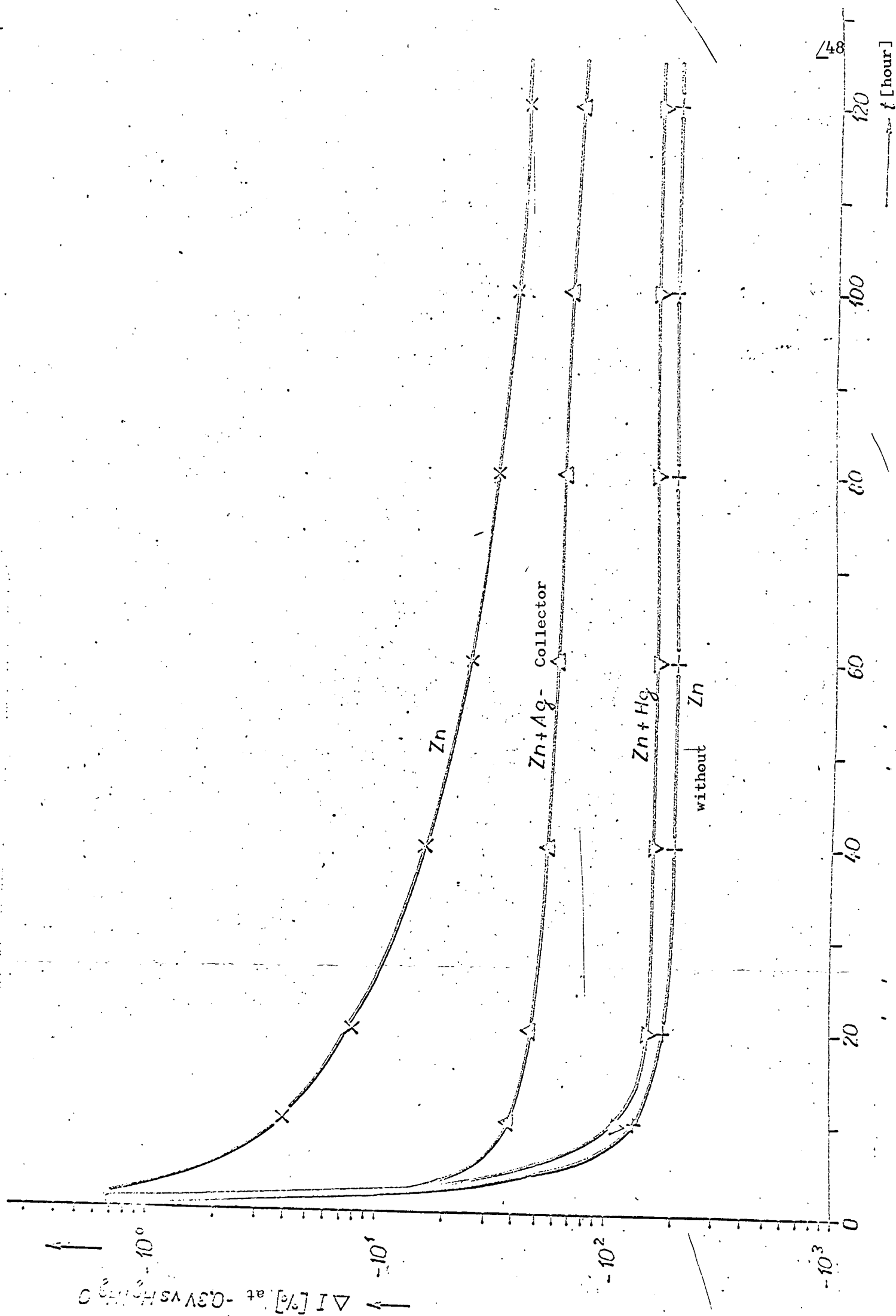


Figure 18. Effect of Zn on retardation of the oxygen electrode activity decrease under zero-load conditions without oxygen pressure.

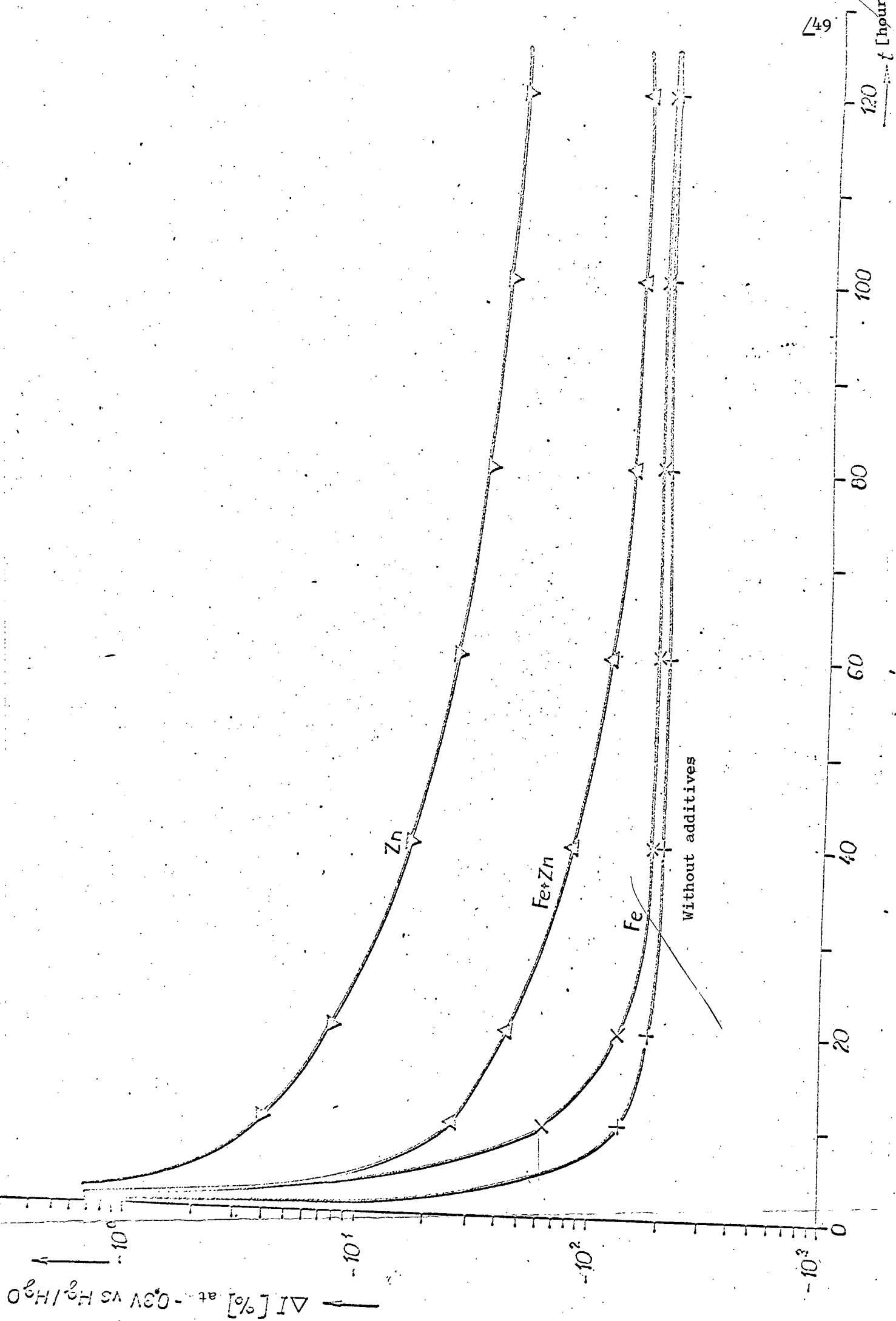


Figure 19. Effect of Zn on retardation of the oxygen electrode activity decrease under zero-load conditions without oxygen pressure.

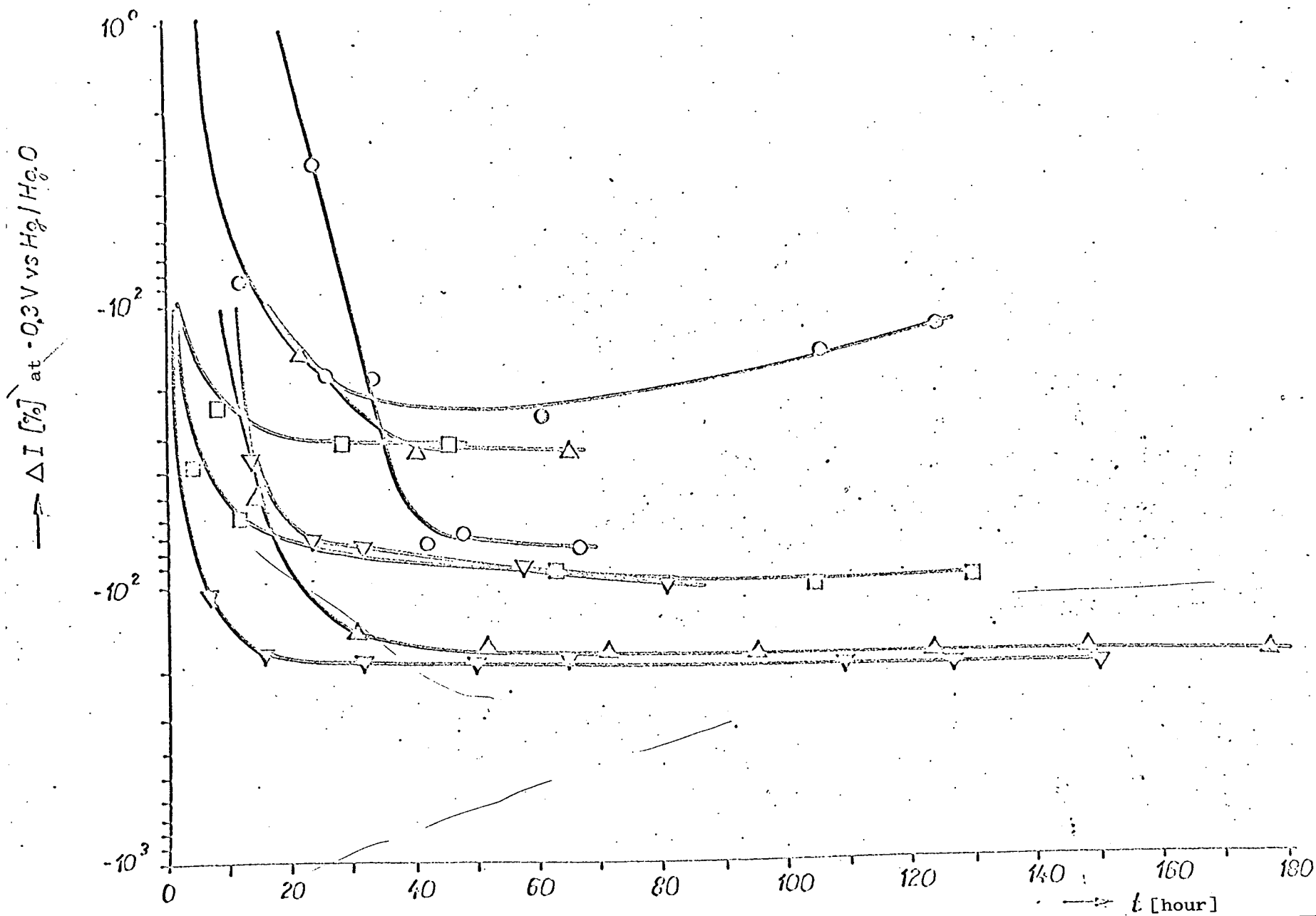


Figure 20. Effect of CO_3^{2-} on the oxygen electrode activity.

Materials that were investigated from the point of view of the effect on the silver catalyst activity may be divided into the following groups:

a) Materials substantially lowering the activity of the Ag-catalyst
 Ag^{I} present in a dissolved form in the alkaline electrolyte as a
complex anion, e.g. $[\text{Ag}(\text{OH})_2]^-$.

b) Materials that do not retard the decrease of the Ag catalyst activity
caused by the influence of Ag^{I} in the form of complex anions

This property was discovered in Hg used to amalgamate the Ag catalyst in the prepared oxygen electrode and also in zincates, cadmates, ferrates and nickelates.

c) Materials that retard the decrease of the silver catalyst activity
caused by the influence of Ag^{I} in the form of complex anions

From among the investigated materials, the following may be included into this group: Ni, Cd, Fe, amalgamated Zn used in the metallic form, and CO_3^{2-} as an electrolyte component. It is possible to assume on the basis of the literature data given in Section 2 that the above-mentioned anions, with the exception of zincates, will also have a negative effect on the decrease of the silver catalyst activity. This effect is certainly less important than the effects listed in paragraph a) above. It is possible to assume that the effects due to these anions would come to light if the "self poisoning" by silver were sufficiently suppressed.

d) Materials that substantially retard the decrease of the Ag catalyst
activity caused by the influence of Ag^{I} in the form of complex anions

Among the materials investigated materials only metallic Zn fits into this category.

It is evident from the preceding survey that we have not found a material to date that would prevent the loss of the silver catalyst activity of the investigated oxygen electrode based on the system Ag catalyst-macromolecular material in the zero-load state.

6. Closing statements

Since from the present economic point of view, it is impossible to use a different catalyst than silver as the catalyst for the electrochemical re-

duction of oxygen at the cathode in an alkaline medium, our results as well as those of other authors confirm that increased attention should be devoted to the investigation of the phenomena that affect the silver catalyst of the oxygen electrode in the zero-load state.

On the basis of the results obtained from our work we are led to the conclusion that it is above all necessary to seek ways for the prevention of the formation of Ag^{I} present in the form of complex anions in the electrolyte at all stages of the oxygen electrode activity.

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- Figure 1. Dependence of the solubility of Ag_2O on the KOH concentration at 25°C [4].
 X - Solubility of Ag_2O at 25°C [4].
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 Δ - 0.01 M
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 O - 0.001 N
 Δ - 0.005 N
 □ - 0.01 N
 X - 0.03 N
 O - 0.09 N
- Figure 10. Adsorption changes (expressed as degrees of polarization) at the platinum electrode surface for NaCl solutions determined by ellipsometric method [33].
 O - 3×10^{-4} M
 Δ - 1×10^{-3} M

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$\square - 5 \times 10^{-3} \text{ M}$
 $\circ - 1 \times 10^{-2} \text{ M}$
 $\Delta - 2 \times 10^{-2} \text{ M}$

Figure 11. Effect of zero-load oxygen electrode state with and without oxygen pressure on its activity loss in electrolytes containing no Ag^{I} at the start of experiment.

with O_2	without O_2	
Δ	Δ	7 N NaOH
\square	\square	7 N KOH
\circ	\circ	7 N NaOH without CO_3^{2-}

Figure 12. Effect of zero-load oxygen electrode state with and without oxygen pressure on its activity loss in electrolytes containing Ag^{I} at the start of experiment.

with O_2	without O_2	
Δ	Δ	7 N NaOH + Ag^{I}
\square	\square	7 N KOH + Ag^{I}

Figure 13. Effect of Ag collectors and leads on lowering of the electrode activity under zero load and with complete immersion.

Δ 7 N NaOH	Ag-collector and leads
Δ 7 N KOH	
\square 7 N NaOH	Pt-collector, Ag-leads
\square 7 N KOH	
\circ 7 N NaOH	Pt-collector and leads
\circ 7 N KOH	

Figure 14. Change of Zn-PTFE electrode potential under the influence of Ag^{I} present as $[\text{Ag}(\text{OH})_2]^-$ in 7 N KOH electrolyte in $4.8 \cdot 10^{-4} \text{ N}$ concentration.

Figure 15. Effect of polarization and zero load without oxygen pressure on activity decrease of oxygen electrode.

polarization	immersion	
Δ	Δ	7 N KOH
\square	\square	7 N NaOH

▽	▽	7 N NaOH without CO_3^{2-}
0	0	7 N NaOH + 19.5% CO_3^{2-}

Figure 16. Effect of Zn, Cd, and Fe on the oxygen electrode zero-load state without oxygen pressure.

+ in absence of metals
 ▽ Fe
 X Cd
 Δ Ni
 0 Zn

Figure 17. Effect of oxygen electrode amalgamation on its activity decrease without oxygen pressure under zero-load conditions. /57

+ without amalgamation
 X amalgamation of electrode before use
 Δ amalgamation of electrode 40 hours after loading.

Figure 18. Effect of Zn on retardation of the oxygen electrode activity decrease under zero-load conditions without oxygen pressure.

+ in absence of Zn
 ▽ Zn - amalgamated
 Δ Zn + Ag-collector
 X Zn - unamalgamated

Figure 19. Effect of Zn on retardation of the oxygen electrode activity decrease under zero-load conditions without oxygen pressure.

+ in absence of metals
 X Fe
 Δ Fe + Zn
 ▽ Zn

Figure 20. Effect of CO_3^{2-} on the oxygen electrode activity.

Δ	Δ	7 N NaOH without CO_3^{2-}
□	□	7 N NaOH + 1.5% CO_3^{2-}
0	0	7 N NaOH + 9.5% CO_3^{2-}
▽	▽	7 N NaOH + 19.5% CO_3^{2-}

1. Austin, L. G., Fuel Cells, NASA SP-120.
2. Bockris, J. O'M., Damjanovic, A. and McHardy, J., Proc. "Troisiemes Journees Internation. d'Etude des Piles a Combustible", SERAI, Brussels (1969).
3. Schwartz, H. J. and Ward, J. J., NASA SP-5057, Selected Technology for the Electric Power Industry, Conference Arranged by NASA-Lewis Research Center, Cleveland, Ohio, September 1968, p.281.
4. Koba, L. D., Balashova, N. A., Zh. neorg. khim., 4, 225 (1959).
5. Laue, F. Z., Z. anorg. chem., 165, p. 325 (1927).
6. Dirkse, T., Vander Lugt, L., J. Electrochem. Soc., 111, p. 629 (1964).
7. Rile, J., NASA ASD-TDR-63-560 (AD-418 143).
8. Young, G. J., Fuel Cells, London, 1960.
9. Wagner, C. C., J. Electrochem. Soc., 116, p. 5 (1969).
10. Klemm, W., Angew. Chem., 66, p. 407 (1954).
11. Jasinski, R., High Energy Batteries, Plenum Press, New York, 1967, p. 75.
12. Caines, L., J. Electrochem. Soc., 116, No. 2, p. 610 (1969).
13. Amlie, R. F., Ruetschi, P., J. Electrochem. Soc., 108, No. 9, p. 813 (1961).
14. Dirkse, T., J. Electrochem. Soc., 106, p. 453, (1959).
15. Panel Discussion, "Nature of Ag⁰", Soc. Meeting, Buffalo, N. Y., 1965.
16. Lander, A., Patton, J. T., J. Electrochem Soc., 114, p. 113 (1967)
17. Hammer, W. J., Craig, D. N., J. Electrochem. Soc., 104, p. 206 (1957).
18. Bork, J. F., Carrett, A. B., J. Electrochem. Soc., 106, p. 612 (1959).
19. Giles, R. D., Harrison, J. A., Thirsk, H. R., J. Electroanal. Chem., 22, p. 375 (1969).
20. Neiding, A. B., Kazarnovskii, I. A., Dokl. akad. nauk SSSR, 78, p. 713 (1951).
21. Cahan, B. D., Ockerman, J. B., Amlie, R. F., Ruetschi, P., J. Electrochem Soc., 107, p. 725 (1960).

22. Ohse, R. W., Z. elektrochem., 63, p. 1063 (1959).
23. Wales, C. P., Burbank, J., J. Electrochem. Soc., 112, p. 13 (1965).
24. Wales, C. P., Simon, A. C., NASA Contract DC 20360, May 1968.
25. Johnston, H. L., Cuta, F., Carrett, A., J. Amer. Chem. Soc., 55, p.231 (1933).
26. Pleskov, Y., Kabanov, S., Zh. neorg. khim., 2, p. 1807 (1957). /58
27. Visco, R. E., Renner, R. H., Extended Abstracts of the Battery Division Electrochem. Soc., 14, Abstract No. 7, Detroit, Mich., 1969.
28. Brezina, M., Koryta, J., Musilova, M., Collect. Czech. Chem. Commun., 33, p. 3397 (1968).
29. Jansta, J., Dousek, F. P., "Time Changes of Electrochemical Properties of the Hydrophilic Three-Phase Catalytic Porous Electrodes", Proc. 21st Meeting Intern. Com. of Electrochem. Thermodynamics Kinetics (CITCE), Praha (1970).
30. Giles, R. D., Harrison, J. A., J. Electroanal. Chem. Interfacial Electrochem., 24, No. 23, p. 399 (1970).
31. Bockris, J. O'M., et al., Report N 68-18217, NASA CR-93364, March 1968.
32. Bockris, J. O'M., Ying-Chech Chiu, Genshaw, M., Report N 69-25396, NASA CR-100 892, January-June 1968.
33. Bockris, J. O'M., Paik, W. K., Genshaw, M., Report N 69-25397, NASA CR-100893, July-December 1968.
34. Sandera, J., et al., Vyzkumna zprava z r., Research Communication , Department of Electrotechnology, FE-VUT Brno, 1969.
35. Williams, K. R., Ed., An Introduction to Fuel Cells, Elsevier Publishing Co., Amsterdam, 1966.
36. Jansta, J., Chem. Listy, 61, p. 519, 617 (1967).
37. Arcand, M. G., NASA Report N 69-21172, Contract No. NAS 7-100, Nov. 1969.
38. Arcand, M. G., NASA Report N 69-21064, Contract No. NAS 7-100, Feb. 1969.
39. Kabanov, B. N., Electrochim. Acta, 13, p. 19 (1968).
40. Aleksandrova, O. P., Kisseleva, I. G., Kabanov, B. M., Zh. Fiz. Khim., 38, p. 811 (1968).
41. Kiseleva, I. G., Tomashova, N. N., Kabanov, B. N., Zh. Fiz. Khim., 38, p. 648 (1968).
42. Tomashova, N. N., Astakhov, J. J., Kiseleva, I. G., Kabanov, B. N., Elekrokimiya, 4, 1143 (1968).

43. Shumilova, N. A., Zhutayeva, G. V., Tarasevich, V. J., Electrochim. Acta, 11, p. 967 (1967).
44. Zhutayeva, G. V., Shumilova, N. A., Elektrokhimiya, 4, p. 87 (1968).
45. Zhutayeva, G. V., Shumilova, N. A., Luk'yanicheva, V. I., Elektrokhimiya, 4, p. 168 (1968).

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